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SEMI-COMMERCIAL TRIALS ON RADIATION PRESERVATION OF POTATOES UNDER TROPICAL CONDITIONS

ISMAIL KHAN, MOHAMMAD WAHID, ABDUS SATTAR and MOHAMMAD JAN

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Accepted for Publication April 30, 1986

ABSTRACT

Four potato varieties–Cardinal, Desiree, Multa and Patrones were tested by irradiating at 0.10 kGy and subsequent storage for 2 months at 20°C and ambient conditions (30–45°C). The results revealed that rotting during 2 months was markedly more in potatoes stored at ambient temperatures (60–85%) than at 20°C (3–5%) depending on the variety. The weight loss ranged 12–40% at ambient conditions and 4–11% at 20°C. Influence of storage temperatures on reducing sugars, ascorbic acid and sensory scores was variable. Radiation treatment inhibited sprouting, slightly increased the rot and ascorbic acid losses, decreased weight loss and improved the sensory quality of potato chips. In a subsequent semi-commercial trial involving 8 tons of Cardinal and Patrones potatoes carried out at 20°C, there was higher rot (20–45%) and weight loss (28–51%) in unirradiated than in irradiated samples having rot 17–40% and weight loss 20–30% during 6 months storage. Effect of radiation and storage was severe on ascorbic acid but negligible on sugars. Sensory quality was improved as a result of radiation treatment. The data on transportation trial showed higher losses in using jute-bags and truck than wooden crates and railway train. The cost economics for food irradiation based on a source strength of 100 kCi was Rs.60.0 ($4.0) per ton.

INTRODUCTION

Potato is the most important vegetable which occupies a prominent position among the food crops cultivated in Pakistan. It is grown in almost all provinces of the country. Storage of potatoes is a serious problem especially during the humid hot summer months, April to September. About 25% of the produce is estimated to be stored in the cold storages (3–4 °C) and the remaineder is either marketed immediately after harvest or stored for short duration under ambient

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conditions (30–45 °C). There are no exact estimates of the postharvest losses, however, it is believed that the deterioration of potatoes amounts to well over 10–20% in Pakistan (Khan and Muhammed 1975) and 20% in India (Thomas *et al.* 1979). Chemical sprout inhibitors are not used in Pakistan. Influence of irradiation on the storage quality of potatoes under temperate or subtropical conditions has been extensively studied (Khan 1982; Thomas 1982) whereas little information is available on semi-commercial studies on radiation preservation of potatoes under tropical conditions such as in Pakistan. Laboratory scale experiments on the preservation of potatoes have been conducted in Pakistan and other countries but available data are insufficient to justify the feasibility of radiation technology on a semi-commercial scale.

In view of these problems the present study was conducted during 1982–84 to test the feasibility of radiation technology in the preservation of potatoes on semi-commercial scale.

MATERIAL AND METHODS

Four commercially important varieties of potatoes grown in North Western Frontier Province of Pakistan were used in these studies. They were sown in experimental farm of the Institute during January and harvested in April each year for the experiment. After harvesting the produce was stored in the Institute for 2–3 weeks under ambient conditions before radiation treatment.

During 1982 about 400 kg of each variety (Cardinal, Desiree, Multa and Patrones) were used and half of the samples were irradiated in Co–60 irradiator (Gamma bean 650) at ambient temperatures of 28–32 °C at a dose of 0.10 kGy. The radiated and unirradiated potatoes were stored after packing in wooden crates in a cold room maintained at 20° ±2 °C (R.H. 50–70%) and ambient conditions, 30–45 °C (R.H. 40–50%). Treated and untreated potatoes were examined during storage for rot, weight loss and sprouting and analyzed for ascorbic acid, reducing sugar and sensory tests were also performed.

On the basis of performance of different varieties during the experiment, only two varieties i.e. Cardinal and Patrones were selected for the experiments during 1983 and 1984. About 2000 kg of each variety were used each year, out of which half of the material was irradiated at 0.10 kGy dose in Co–60 gamma irradiator having a dose rate of 0.96 Mrad/h. Radiated and unirradiated samples were kept at 20°±2 °C (R.H. 50–70%). For transportation trial, 400 kg each of irradiated and unirradiated potatoes for different modes (truck and train) and different packaging materials (jute bags and wooden crates) were used. Radiated and unradiated potatoes were transported to Faisalabad and brought back to NIFA, Peshawar, covering almost a distance of 1000 km. These potatoes were again stored at 20°±2 °C for further evaluation. The incidence of rot, weight loss and sprouting as well as other biochemical assays were done.

Reducing sugars were determined by spectrophotometry (Ting, 1956). Ascorbic acid was determined by titrimetry according to AOAC (1970). Organoleptic evaluation of potato chips and boiled potatoes was carried out according to the Hedonic scale ratings, a preference sensory test (Larmond 1977). In order to test the consumer's acceptability of radiated and unirradiated potatoes, 6 families, having 5 members each, were randomly selected and were requested to furnish mean ratings for colour, texture and taste of potato chips and boiled potaotes.

RESULTS AND DISCUSSION

The results revealed that the rot attack markedly increased throughout the successive storage intervals. The percentage rot was lesser at low temperatures than at room temperatures and this pattern was obvious throughout the storage. At the end of 8 weeks, the rot in potatoes at low temperatures ranged 3.0–7.0% in the control and 4.0–8.1% in the irradiated samples indicating practically insignificant differences between the treatments as shown in Fig. 1. At room temperature, the rot-attack ranged 60.0–83.7% in the control and 68.0–85.5% in the radiated samples of all varieties which shows significant influence of temperature on the rotting of potatoes. Comparative susceptibility data at low temperature storage indicated the following general order of rot-susceptibility among the varieties studied; Multa > Desiree > Cardinal > Patrones.

The effect of irradiation and storage on weight loss, ascorbic acid and reducing sugars is shown in Fig. 2. and 3 and Table 1. The results revealed that weight loss was more at room as compared to low temperature storage, which is obviously due to rapid moisture loss at ambient storage conditions. Highest weight loss (30.6–51.7%) was found in the treated and untreated Multa potatoes and the lowest was in the Patrones (21.8–30.2%). Rapid ascorbic acid losses were found as a result of 24 weeks storage in all the varieties which amounted to approximately 50% in many cases as shown in Fig. 3. The losses in the ascorbic acid as a result of radiation were relatively higher. The data on reducing sugars revealed irregular effect of radiation (Table 1). In order to make an estimation of dispension of the amount of reducing sugars in relation to the irradiation treatment the coefficient of variation was measured. This revealed small differences during initial storage and wide differences in the reducing sugars during later storages.

Sensory quality of treated and untreated potatoes in the forms of boiled-potaotes and potato-chips after eight weeks storage of all the varieties, was also determined. It was found that the varieties Desiree and Cardinal performed better as compared to Multa and Patrones in the form of boiled product at both the storage temperatures. In the form of potato-chips, the radiated products invariably scored higher for all the parameters almost in every variety.

It has been reported that gamma radiation dose of 10 Krad completely suppressed sprouting regardless of storage temperature and that storage of ir-

Table 1. Effect of irradiation and storage on the reducing sugars (g/100g) content of potatoes

Varieties	Storage periods (months)						
	0	1	2	3	4	5	6
Cardinal							
Control	1.39	1.32	1.28	1.15	1.03	0.95	0.86
Radiated	1.43	1.30	1.42	1.20	0.67	0.99	0.67
Desiree							
Control	1.39	1.36	1.35	1.00	0.64	0.70	0.76
Radiated	1.39	1.37	1.35	1.15	0.96	0.75	0.92
Multa							
Control	1.35	1.34	1.32	1.17	0.49	0.50	0.84
Radiated	1.35	1.35	1.35	1.21	0.86	0.62	0.76
Patrones							
Control	1.53	1.45	1.50	1.18	0.85	0.87	1.16
Radiated	1.55	1.47	1.56	1.21	0.96	0.99	1.26
C.V.							
Control	5.37	4.19	7.06	7.47	31.46	26.35	19.34
Radiated	6.01	5.18	6.97	2.41	15.81	21.98	28.71

Storage temperature = 20±2°C

radiated potatoes under tropical temperatures is not feasible due to bacterial spoilage (Thomas *et al.* 1979). However, irradiated tubers can be stored with reduced losses (7–30%) for 5–6 months at 10–15 °C. Losses between 25% and 65% of the initial weight, depending on the variety, have been reported for potatoes stored for 6.5 months in a semi-subterranean soil in Colombia (Booth 1974). Greater losses amounting to complete storage failure are known to occur under tropical conditions (Booth and Proctor 1972).

Influence of irradiation on rot, weight loss sprouting, ascorbic acid, sugars and sensory tests was studied every month during the storage period of 6 months at 20 °±2 °C. The rot attack and weight loss increased during storage. Extent of rot was more in Cardinal than in Patrones throughout the storage period. However, the differences between treated and untreated samples were inconsistent. After 6 months storage, the rot ranged 22.0–25.3% in Cardinal and 16.2–18.0% in Patrones, irrespective of radiation treatments. Percentage of weight loss was comparatively higher in unirradiated (28–52%) than irradiated (20–30%) potatoes whereas varietal differences were marginal. Gamma irradiation at 0.10 kGy completely suppressed sprouting regardless of variety.

Ascorbic acid contents decreased markedly during successive storage and the loss was more in irradiated than unirradiated potatoes. However, the pattern of change in reducing sugar was generally irregular. Allen *et al.* (1978) also reported that in some potato varieties the period of low temperature induced an earlier onset of sprout growth and increased total and individual sprout length per tuber, whereas in others the period of cold did not hasten the onset of sprouting but markedly increased the number of growing sprouts and total sprout length. Burton and Wilson (1978) found that mature tubers stored at 10 °C always showed an initial rise in reducing sugars. The increased sugar contents decreased on transfer to 20 °C. The start of sprout growth at 10 °C did not result in sugar accumulation during subsequent storage at 20 °C. However, Verma *et al.* (1974) reported that potato tubers stored in a farm at 24.7 °–36.2 °C accumulated considerable quantities of total sugars. Sucrose was found to be the main component, though in the variety Kufri Chandramukhi, reducing sugars accumulated in amounts equal to sucrose.

Influence of irradiation, packaging materials (jute bags and wooden crates) and mode of transportation (truck and train) on percentage rot during storage for 6 months at 20 °C was studied. The data, as shown in Table 2, revealed markedly higher potato rot in jute bags (26.4–29.4%) than wooden crates (11.79–18.7%), depending on the variety, during transportation by road. Similarly the rot percentage varied from 13.5 to 17.5 in jute bags and 5.9 to 7.1 in wooden crates when the samples were transported by train. Determination of the C.V. indicated wider differences in rotting among unirradiated and irradiated potatoes when transported in the train than those in the truck. Determination of C.V. is specially appropriate under conditions where there are ex-

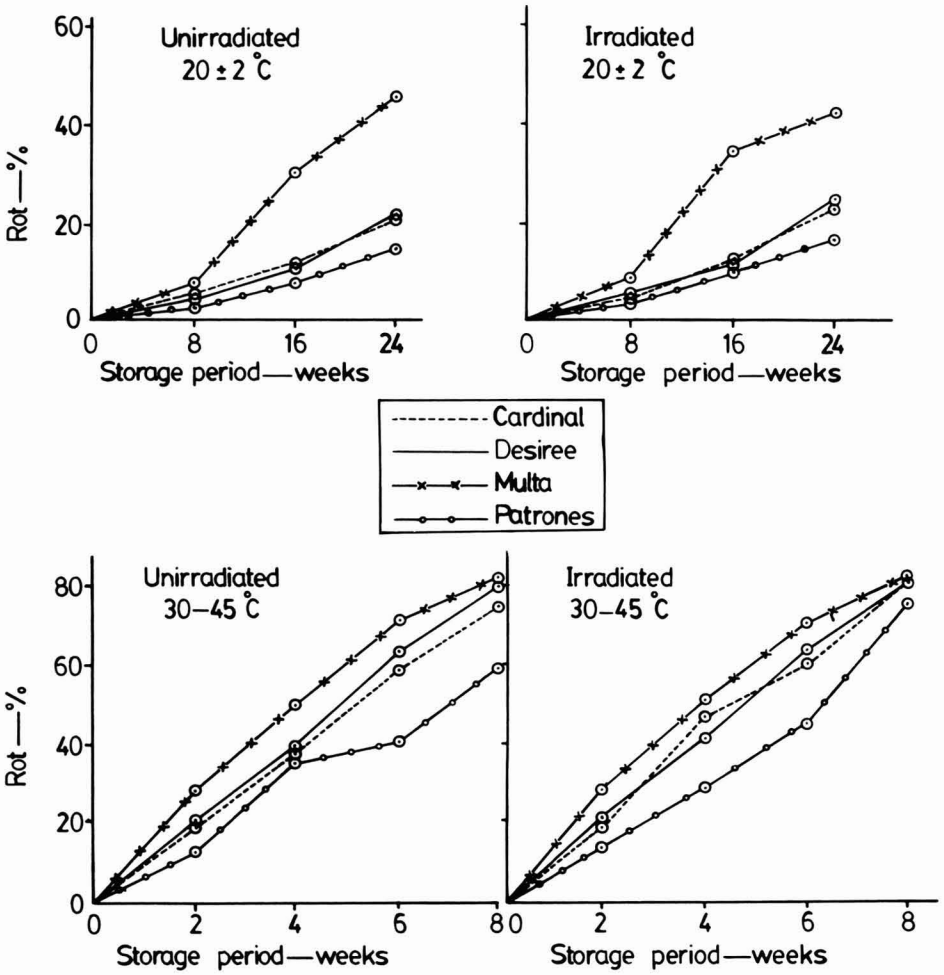

FIG. 1
EFFECT OF IRRADIATION AND STORAGE TIME AND TEMPERATURE ON PERCENTAGE ROT OF DIFFERENT POTATO VARIETIES

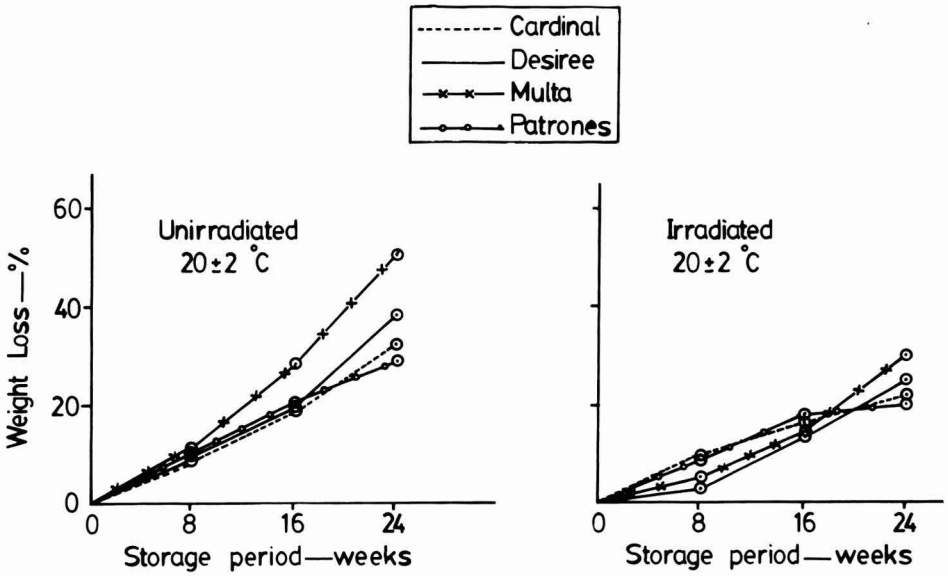

FIG. 2
EFFECT OF IRRADIATION AND STORAGE ON WEIGHT LOSS OF DIFFERENT POTATO VARIETIES

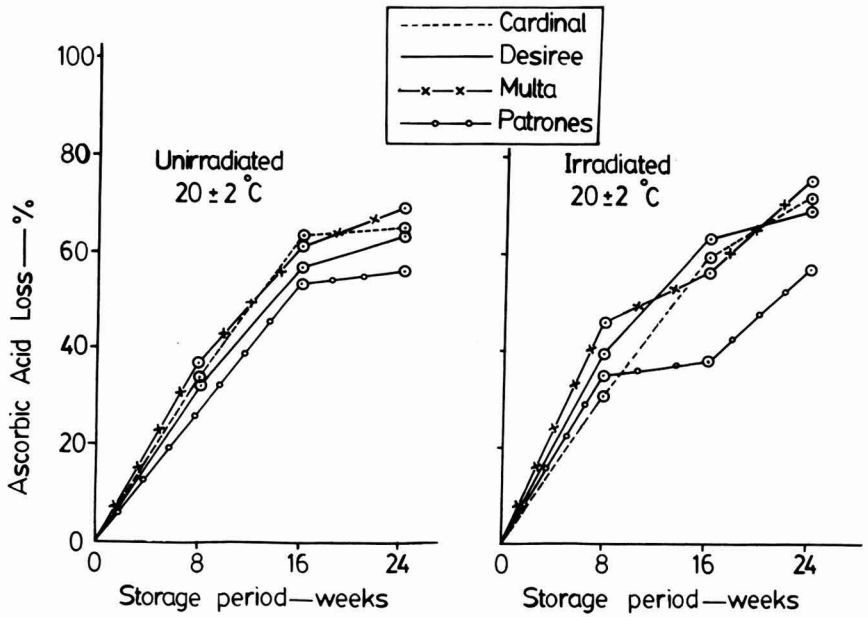

FIG. 3
EFFECT OF IRRADIATION AND STORAGE TIME ON ASCORBIC ACID LOSS OF DIFFERENT POTATO VARIETIES AT 20±2 °C

Table 2. Effect of mode of transportation on the percentage rot of potatoes during 6 months storage

Variety / Treatment	Mode of Transportation			
	Truck-Road		Railway-Train	
	Jute-bags	Wooden-Crates	Jute-bags	Wooden-Crates
Cardinal				
Control	26.4	17.4	17.5	5.9
Irradiated	27.5	18.7	16.2	6.4
Patrones				
Control	29.4	11.9	13.5	6.5
Irradiated	28.2	13.7	14.5	7.1
C.V.				
Control	7.59	26.48	18.19	6.78
Radiated	1.76	23.79	7.82	7.32

Storage temperature = 20° ±2°C

treme values or when it is desired to express variation as a percentage of the average around which the deviations are taken.

The sensory evaluation revealed that quality of potatoes with regard to products such as boiled-potatoes and potato-chips decreased during the storage in both the varieties. Irradiated samples in the forms of potato-chips invariably scored higher than the corresponding controls (Table 3). However, slight darkening was observed in the irradiated boiled potatoes during 3–6 months storage. Baerug and Enge (1974) found a significant but less strong relationship between tuber color and potassium content of tubers. An increase in enzymic browning and after cooking discoloration took place during the first 3 months of storage but not during the next 3 months. Less enzymic browning occurred after 3 months of storage at 12 °C than at 3 °C. It has been reported earlier that potatoes exposed to 10 Krad of gamma rays for sprout inhibition tended to develop after-cooking darkening, after storage at 15 °C for over 3 months (Thomas *et al* 1979; Thomas 1982). Schippers (1975) found that chip color of potatoes deteriorated more during storage at low temperature (5 °C) than higher temperature (12.5 °C). Storage of potatoes at 100% R.H. resulted in significant dark color of chips than at 70–80% R.H.

Table 3. Effect of irradiation and storage on the consumer acceptability of potato products

Varieties	Appearance			Texture			Taste		
Months	2	4	6	2	4	6	2	4	6
Potato chips									
Cardinal									
Control	7.0	6.7	5.2	7.0	6.4	4.8	7.6	6.6	4.8
Radiated	7.6	8.1	6.6	7.2	7.2	6.0	8.2	7.0	5.6
Patrones									
Control	7.0	5.7	5.8	6.5	5.4	5.0	8.0	5.6	5.3
Radiated	7.8	6.5	6.9	6.8	6.2	5.7	8.6	6.4	6.5
Boiled potatoes									
Cardinal									
Control	6.8	6.2	5.5	6.8	5.5	6.6	6.4	6.8	4.6
Radiated	6.7	6.0	5.6	6.9	6.0	5.0	6.7	6.2	4.5
Patrones									
control	7.9	7.0	4.6	7.2	6.6	4.9	6.9	6.6	4.9
Radiated	7.0	7.0	4.0	7.0	6.0	5.0	6.7	6.5	4.5
C.V.									
Control	6.83	8.91	9.68	4.22	10.22	10.05	9.87	8.44	5.92
Radiated	7.04	13.01	22.53	2.44	4.55	25.29	12.55	6.48	18.22

Storage temperature = 20°±2°C
Hedonic scale rating 10 = Extremely liked
1 = Extremely disliked

Total production of potatoes and onions in the North West Frontier Province of Pakistan, where this Institute is located, was estimated to be 101,000 tons and out of this one third produce was considered to be available for irradiation whereas the rest for fresh consumption. The cost economics of food irradiation was calculated for a source strength of 100 kCi and throughput rate of 20 tons per hour. The annual cost estimated as Rs. 2040,000 included the capital (10% of total) and other operational expenses. On the basis of the production and expenditure involved, the cost for irradiation potatoes was found to be about Rs.60.00 ($ 4.0) per ton. The cost could further be reduced if more food items are included for irradiation. Economic feasibility of radiation preservation of potatoes, garlic and onions in Pakistan has been reported earlier by Khan and associates (1975, 1978, 1984).

CONCLUSIONS

It is concluded that irradiation followed by storage at 20 ± 2 °C (R.H. 50–70%) is the optimum condition to store potatoes for about 6 months with minimum rot attack and quality losses. The Patrones variety was found better than Cardinal, Desiree and Multa during storage. Irradiated samples in the form of potato chips scored higher than respective controls. The results regarding transportation trial involving different containers and mode of transportation indicated significantly higher losses in using jute bags and truck than wooden crates and train. The approximate cost of irradiating potatoes at a dose of 0.1 kGy from a source strength of 100 kCi was determined to be Rs.60.0 (US $ 4.0) per ton.

ACKNOWLEDGMENTS

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INFLUENCE OF REACTION CONDITIONS ON FORMING NON-DIALYZABLE MELANOIDINES FROM GLUCOSE AND GLYCINE

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ABSTRACT

The influence of temperature, time, molar ratio of reagents and water on the formation and the spectral characteristic of non-dialyzable melanoidines of the model system D-glucose-glycine has been studied.

It has been established that the optimum conditions of obtaining nondialyzable melanoidines are: glucose 1M; glycine 0.68 M; temperature 110°C; reaction time 7 h; water content 15%.

The rate constants $4.55 \cdot 10^{-5}$ S^{-1} and $9.40 \cdot 10^{-1}$ S^{-1} for the molar ratio of 2.5:1 and 1:2.5 respectively, have been determined as well.

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INTRODUCTION

In a previous work (Obretenov *et al.* 1981) we have shown that the interaction between glycine and glucose at 95 °C yielded melanoidines with different spectral characteristics. Their isolation has afforded the opportunity of obtaining them in preparation form and submitting them to various examinations and study. We have been interested in studying the influence of temperature, time, molar ratio and water on their preparation and on the spectral characteristic of nondialyzable melanoidines as well as in determining some kinetic parameters of the reaction. The results obtained are the subject of the present discussion.

MATERIALS AND METHODS

Crystalline glucose and glycine with a p.a. qualification have been used for the experiments. The Sephadex gels have been produced in Uppsala, Sweden.

The reaction between glycine and glucose in the presence of water was carried out in a glycerol bath with refluxing and stirring. The reaction mixture was dialyzed through a cellophane membrane for 96 hours against distilled water. The optimum duration of dialysis was determined experimentally. The nondialyzable part was concentrated using a rotational vacuum evaporator at a temperature lower than 30 °C, dried under vacuum and stored in a dark place in an inert atmosphere.

The amounts of water soluble and insoluble melanoidines were determined by full extraction with water at 50 °C. The water extract was evaporated to dryness under the conditions described, dried and stored. Nitrogen content was determined by Kjeldahl. Gel-chromatography of melanoidines was carried out on Sephadex G-50 (column 800 × 20 mm, rate of elution with distilled water – 100 cm^3/h, V_0 against blue dextran – 70 cm^3).

The UV-spectra of the water soluble melanoidines were recorded with a Specord UV-Vis apparatus, Karl Zeiss, Jena.

IR-analyses were carried out in tablets of potassium bromide at equal weight concentrations using a UR-20 apparatus, Karl Zeiss, Jena.

Data processing was performed with standard programs for processing experimental results by the method of least squares, written in FORTRAN-4 and performed by computer -CM-2 (Brandt 1970).

RESULTS AND DISCUSSION

The choice of an appropriate method for isolating and purifying the melanoidines was a matter of particular importance. The melanoidines should be fully separated from glucose, glycine and low molecular products which have

not reacted. Moreover, the method chosen should be feasible and possess a high degree of reproducibility as well. We have chosen to separate the reactants from the melanoidines by precipitation with ethyl alcohol, gel-chromatography and dialysis. Simple precipitation with alcohol does not always ensure the complete removal of the glucose and glycine which have not reacted. The low molecular melanoidines may dissolve in alcohol (Obretenov *et al.* 1981; Enders and Theis 1938). The gel-chromatography and dialysis have both given positive results. The difference in the UV-spectra of the reaction mixture (curve 3) as well as of the purified melanoidines (curves 1 and 2) is shown in Fig. 1. The absence of any maximum at 285 nm which is due to the presence of premelanoidines and the complete identity of the spectra of the purified melanoidines has confirmed the conclusion drawn. In further experiments we have applied dialysis with cellophane and distilled water. Although time consuming, the method does not require the use of gels, it is feasible and yields pure melanoidines. The purity of melanoidines has been established experimentally using a series of different model mixtures of melanoidines, glucose and glycine, which were submitted to dialysis; then we determined the mass of the products dialyzed and submitted them to spectral analyses.

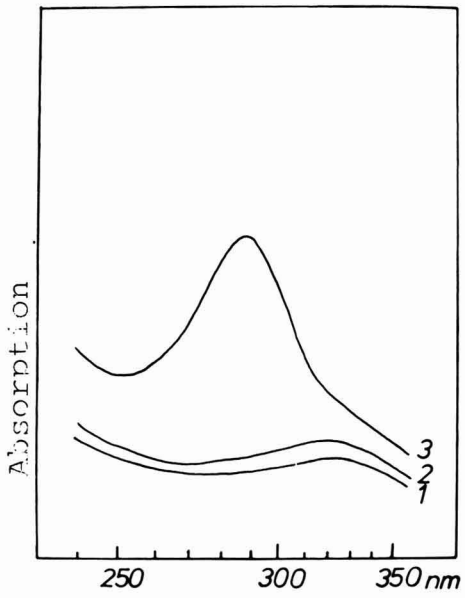

FIG. 1.
UV SPECTRA OF THE REACTION MIXTURE (3) AS WELL AS OF THE POLYMER PRODUCTS, ISOLATED BY GEL CHROMATOGRAPHY (2) AND BY DIALYSIS (1)

The influence of the amount of water, the molar ratio, reaction time as well as the temperature on the yield and the spectral characteristics of melanoidines have been studied experimentally.

Experiments With Different Amounts of Water

A wide range of water content (from 10 to 70%) was chosen for experimentation. The reaction was carried out at 100 °C and a time of 7 h. The temperature and time were selected on the basis of previous work (Obretenov *et al.* 1981). The molar ratio of glucose and glycine was 5:1. The results obtained are given in Table 1.

Table 1. Influence of water content on melanoidine formation during heating

N°	Water content, %	Yield*, g	State of reaction mixture	Solubility of melanoidine in water, %
1.	10	3,23	heterogeneous	80
2.	20	2,53	homogeneous	100
3.	30	1,88	homogeneous	100
4.	50	1,64	homogeneous	100
5.	70	1,60	homogeneous	100

* glucose – 13.50 g, glycine – 1.12 g

The highest yield of nondialyzable melanoidines was obtained at the lowest water content. On increasing the water content, there was almost a twofold decrease in yield. A comparatively wide range for the optimum water content of the Maillard reaction has been given in literature (Wolfrom *et al.* 1974; Orsi *et al.* 1978; Lea and Hannan 1949; Labuza and Shapero 1978; Wolf *et al.* 1977; Herrmann and Nour 1977). In our further experiments, we decided on a 20% water content since the reaction mixture was homogenous and a sufficiently good yield of nondialyzable melanoidines was obtained.

A substantial difference in the UV-spectra of the reaction mixtures and the nondialyzable melanoidines was observed (Fig. 2).

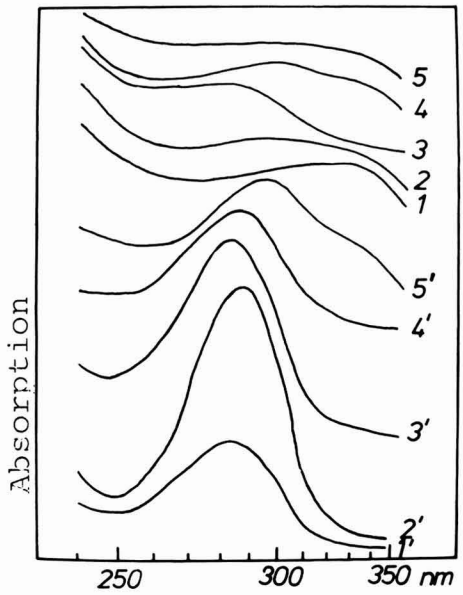

FIG. 2.
UV SPECTRA OF REACTION MIXTURES (1'-5') AND OF THE NONDIALYABLE MELANOIDINES, ACCORDING TO TABLE 1

This fact was expected since premelanoidines with an absorption of about 285 nm were present in the reaction mixtures but were removed via dialysis. On increasing water content from 10 to 30%, the absorption maxima of nondialyzable melanoidines were changed from 325 nm to 290 nm. Then absorption again appeared at 325 nm. At 70% water, melanoidines possessed plateau, like absorption in the range of 290–325 nm. This indicates that lower molecular melanoidines accumulate due to the slowing down of polymerization processes in the experiments with low and high water content (Orsi and Dworschak 1978; Lea and Hannan 1949).

The IR spectra of nondialyzable melanoidines have shown an intensive absorption at 1640 cm^{-1}, characteristic of the carbon-carbon double bond. The absorption of the carbonyl group at 1710 cm^{-1} is weakly expressed. There is a wide absorption band at 1020–1100 cm^{-1} in all spectra due to the deformation fluctuations of the hydroxyl group (Fig. 3).

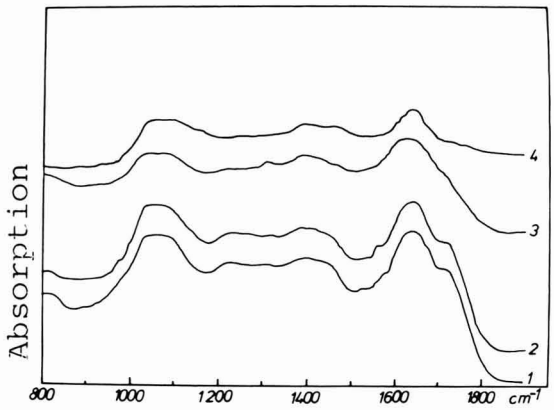

FIG. 3.
IR SPECTRA OF NONDIALYZABLE MELANOIDINES, ACCORDING TO TABLE 1

Experiments With Various Molar Ratios

The molar ratios of reactants chosen and the results obtained are presented in Table 2. The experiments were carried out at 100 °C, for 7 h and at 20% water. Molar ratios outside the range of the ones chosen did not yield homogenous reaction mixtures.

Table 2. Influence of molar ratio on melanoidine formation during heating in 20% water content

N°	Molar ratio glucose:glycine	Amount, g glucose:glycine		Yield, g	State of reaction mixture
1.	5:1	13,50	1,12	2,55	homogeneous
2.	2,5:1	13,49	2,25	3,48	homogeneous
3.	1:1	10,80	4,50	4,94	homogeneous
4.	1:2,5	8,10	8,46	3,60	homogeneous
5.	1:5	5,40	11,26	2,95	homogeneous

The yield of nondialyzable melanoidines was markedly influenced by the reactant concentration when all other conditions were equal. A maximum in melanoidine yield was observed at a ratio 1:1. Since an opinion prevails in literature that the Maillard reaction proceeds in different ways depending on the molar ratio of the amine and the carbonyl component (Dworschak and Orsi 1977; Walfrom *et al.* 1953), then in the further experiments of ours we have worked with the ratios, 2.5:1 and 1:2.5.

All reaction mixtures possessed a maximum of absorption at 285 nm. The absorption at 330 nm increased on increasing glycine concentration. The nondialyzable melanoidines possessed a more strongly expressed maximum of absorption below 300 nm (Fig. 4), compared with the melanoidines, obtained at different water contents (Fig. 2).

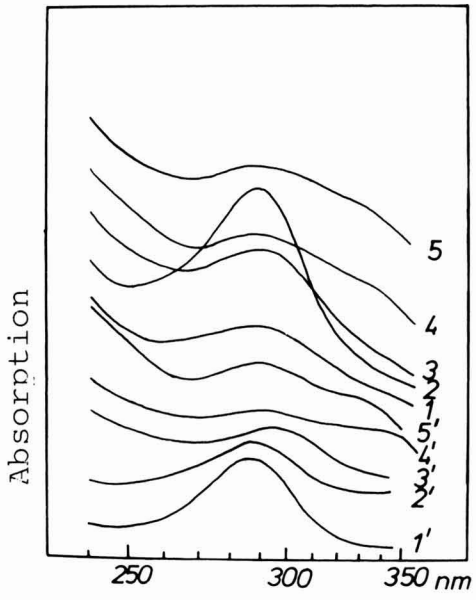

FIG. 4.
UV SPECTRA OF REACTION SYSTEMS (1'–5') AND OF THE NONDIALYZABLE MELANOIDINES, ACCORDING TO TABLE 2

The maximum is more markedly expressed at the higher glucose contents. Probably, under the reaction conditions, greater amounts of furan derivatives were formed, whose inclusion in the melanoidine structrue has an effect on its spectrum. The increased absorption above 300 nm in the experiments with a greater amount of glycine indicates the presence of lower molecular melanoidines, i.e., the slowing down of the polymerization process.

The IR spectra are fully analogous for all nondialyzable melanoidines and similar to those shown in Fig. 3, but the intensity of absorption in the different regions of the spectrum changed.

On increasing the glucose amount, the absorption at 1640 cm^{-1} became much more intensive compared with the absorption at 1020–1100 cm^{-1}. Maxima for the methyl and methylene groups appear at 1380 cm^{-1}.

Experiments at Different Reaction Times

These experiments have been carried out with molar ratios of glucose:glycine 2.5:1 and 1:2.5, temperature 100 °C and 20% water. The results obtained are given in Table 3 and 4. The reaction mixture at the first ratio was homogenous until the seventh hour of interaction (Table 3). The yield of nondialyzable melanoidines increased till the twelfth hour, then it remained nearly constant. The nondialyzable melanoidines were 100% soluble when the reaction proceeded for 1 h, while they become practically insoluble at the end of the interval examined. This fact indicates that the melanoidines increased in molecular mass with duration of reaction time. Nitrogen content did not substantially change and was within the limits of 3.98 to 5.33%.

When the ratio glucose:glycine was 1:2.5, the reaction mixture was the heterogeneous until the third hour of heating due to the incomplete dissolution of reactants. After the twelfth hour it again became heterogeneous due to the accumulation of large amounts of insoluble melanoidines. The maximum yield was achieved at approximately the seventh hour. The reaction proceeded faster, reaching the maximum yield earlier, but the yield was lower compared with the yield at 2.5:1 ratio. Nitrogen content was almost twice as high, compared with the 2.5:1 ratio. The fact that even when the reaction proceeded for 1 h, 44.99% of the total amount of nonidalyzable melanoidines were already insoluble in water points to the acceleration of the reaction (Table 4).

The UV spectra of the reaction mixtures differed substantially from one another (Fig. 5 and 6).

The maximum was clearly expressed and very intenstive at 285 nm in the experiments with an excess of glucose. Conversely, this maximum was weakly expressed in the experiments with an excess of glycine. The absorption was plateau-like and was accompanied by absorption at 330 nm. These spectra indicate that under equal reaction conditions the Maillard reaction proceeded in a rather different way depending on the molar ratio of reagents. After dialysis this

Table 3. Influence of reaction time on the formation of melanoidines (glucose:glycine = 2.5:1)

N°	Reaction time,h	Yield, g	Nitrogen content %	Water soluble melanoidines %	State of reaction mixture
1.	1	0,75	5,33	100	homogeneous
2.	3	2,71	4,45	25,93	homogeneous
3.	5	4,45	4,14	7,10	homogeneous
4.	7	5,68	4,00	4,26	homogeneous
5.	9	5,75	4,70	6,25	heterogeneous
6.	12	7,50	4,37	4,58	heterogeneous
7.	15	7,30	4,48	4,71	heterogeneous
8.	18	7,56	3,98	5,03	heterogeneous
9.	21	6,70	4,45	5,33	heterogeneous

Table 4. Influence of reaction time on the formation of melanoidines (glucose: glycine = 1:2.5)

N°	Reaction time, h	Yield, g	Nitrogen content %	Water soluble melanoidines %	State of reaction mixture
1.	1	1,28	8,67	55,01	heterogeneous
2.	3	3,80	8,33	18,36	heterogeneous
3.	5	4,48	7,60	14,92	homogeneous
4.	7	5,19	7,47	13,79	homogeneous
5.	9	5,20	8,88	12,13	homogeneous
6.	12	5,36	8,71	8,25	heterogeneous
7.	15	5,28	8,30	4,43	heterogeneous
8.	18	5,26	8,43	3,20	heterogeneous
9.	21	5,30	8,80	2,84	heterogeneous

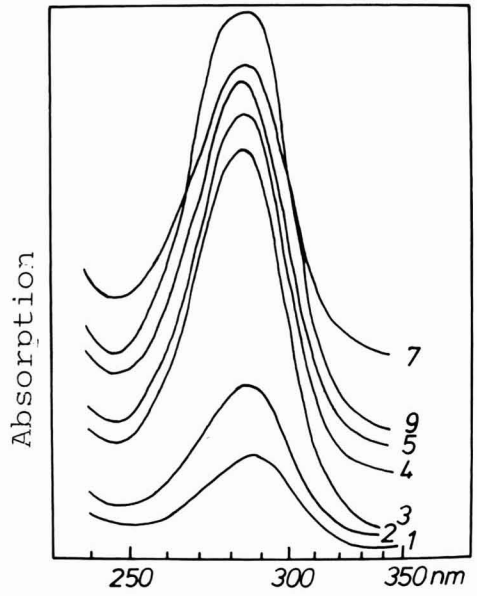

FIG. 5.
UV SPECTRA OF REACTION MIXTURES OF EXPERIMENTS, ACCORDING TO TABLE 3

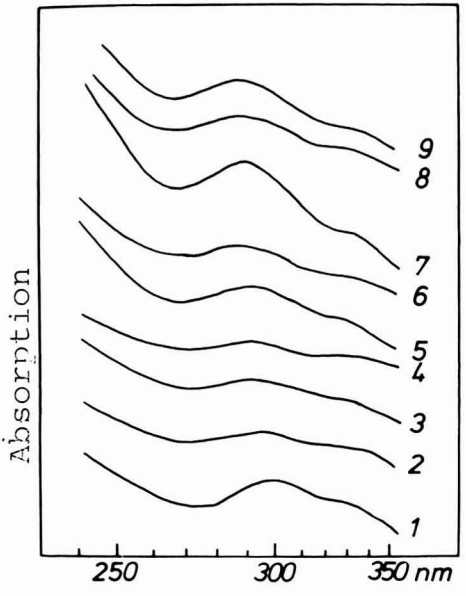

FIG. 6.
UV SPECTRA OF REACTION MIXTURES OF EXPERIMENTS, ACCORDING TO TABLE 4

difference was not as substantial: a well expressed maximum at 290 nm and a weaker absorption at 330 nm were present.

The IR spectra of the nondialyzable melanoidines from the two ratios at different reaction times do not point to any substantial differences except the intensities in the different regions of the spectra.

The IR spectra of the water soluble melanoidines did not differ from those of the total melanoidine product.

Experiments at Different Temperature

These experiments were carried out at the same two ratios as the previous experiment (7 h and 20% water). The data are presented in Tables 5 and 6.

Temperature has a strong influence on the rate of the Maillard reaction. At 100 °C the yield increased approximately 35 times for the first molar ratio (Table 5) and approximately 790 times for the second molar ratio (Table 6) as compared to 50 °C.

These data as well as the previous indicate that with an excess of glycine, the reaction proceeded approximately 2.4 times faster compared with the experiments with an excess of glucose (Table 7).

However, a higher yield was achieved in the second case. Up to 90 °C only water soluble nondialyzable melanoidines were obtained. Nitrogen content was again lower when there was an excess of glucose.

Table 5. Influence of temperature on the formation of melanoidines (glucose: glycine = 2.5:1)

N°	Temperature, °C	Yield, g	Nitrogen content %	Water soluble melanoidines %	State of reaction mixture
1.	50	0,02	4,10	100	heterogeneous
2.	65	0,08	4,17	100	homogeneous
3.	80	1,40	4,83	100	homogeneous
4.	90	3,32	4,31	12,21	homogeneous
5.	100	5,69	4,00	4,26	homogeneous
6.	110	7,06	4,26	4,25	strongly viscous

Table 6. Influence of temperature on the formation of melanoidines (glucose:glycine = 1:2.5)

N°	Temperature, °C	Yield, g	Nitrogen content %	Water soluble melanoidines %	State of reaction mixture
1.	50	0,007	6,20	100	heterogeneous
2.	65	0,10	6,40	100	heterogeneous
3.	80	1,38	6,84	100	heterogeneous
4.	90	3,20	7,68	15,08	heterogeneous
5.	100	5,20	7,87	13,79	homogeneous
6.	110	5,51	8,67	7,51	heterogeneous

Table 7. Kinetic data on the formation of nondialyzable melanoidines

Molar ratio glucose:glycine	A_o, g	K. S^{-1}
2,5:1	7,2636	$4,55.10^{-5}$
1:2,5	5,3364	$9,40.10^{-5}$

The increase in molecular weight of the nondialyzable melanoidines depended on the temperature. Maxima at 300 and 330 nm are evident in both ratios. On increasing the temperature the first one increases in intensity and moves to the left of the spectrum, while the second one disappears or diminishes. The nondialyzable melanoidines have confirmed these dependences, indicating very clearly how the single maximum at 330 nm gradually moves to the left to 290 nm.

The IR spectra do not differ substantially in both ratios at the different temperatures.

The data presented so far offer the possibility of drawing some conclusions on the kinetics of the processes studied. The reaction of melanoidine formation has passed through different stages (Hodges 1953; Obretenov 1983), whose differentiated examination is impossible due to the complete absence of quantitative information about the separate chemical compounds and their molecular mass. This has suggested following the change in yield of nondialyzable melanoidines depending on time. The graphic representation of this change (Fig. 7) is described by the differential Eq. 1

$$\frac{dy}{dt} = C_1 \cdot C_2 \cdot K_1 - y \cdot K_2 \qquad (1)$$

where

y - yield
t - reaction time
C_1 - glucose, g
C_2 - glycine, g
K_1 and K_2 - experimental constants

After solving the equation, the following expression has been obtained:

$$y = A_O(1 - e^{-kt}) \qquad (2)$$

where

A_O - maximum yield, g at a sufficiently long period of time
k - rate constant

Finding A_O and k from the experimental results for both model systems has been done according to the method of least squares (Brandt 1970). The adequacy of estimate of the regression equation was carried out using Pearson's criterion γ^2. The values for A_O and k obtained are given in Table 7.

The data in Table 7 confirm the conclusions drawn that at a glucose:glycine ratio of 2.5:1, the melanoidine formation proceeds at a lower rate but with a higher yield compared with the ratio of 1:2.5.

The lack of any appropriate theoretical model describing the influence of various factors on the reaction yield, has induced us to study the influence of the fundamental reaction parameters according to the method of the full factor experiment (Ruzinov 1980). We have chosen the parameters:

X_1 - water
X_2 - glucose
X_3 - time
X_4 - temperature
X_5 - glycine

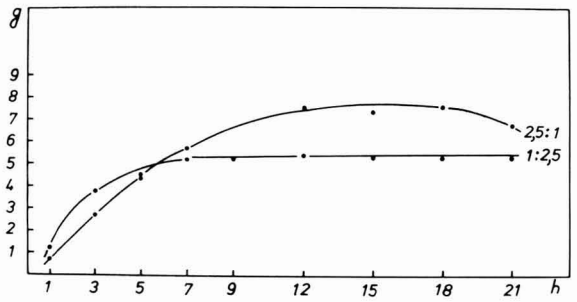

FIG. 7.
CHANGE IN THE YIELD OF THE NONDIALYZABLE MELANOIDINES, DEPENDING ON TIME

We have assumed that the relation between the reaction yield and the factors x_i = 1,2...5 is of a linear type.

$$y = b_0 + b_1 \cdot X_1 + b_2 \cdot X_2 \cdot + b_3 \cdot X_3 + b_4 \cdot X_4 + b_5 \cdot X_5 \qquad (3)$$

The factor change has been coded in advance according to Table 8 using a plan where each of the factors has changed on two levels only.

where

X_i° = a zero level of factor i
ΔX_i = interval of change of factor X_i
$X_i^{\circ} = X_{i\,max} - \Delta X_i = X_{i\,max} + \Delta X_i$
$\Delta X_i = \frac{X_{i\,max} - X_{i\,min}}{2}$

Table 8. Factors, influencing the yield of the reaction

Factors	X_1	X_2	X_3	X_4	X_5
X_i°	20%	10,8039	5	100° C	5,3178
ΔX_i	5%	2,6996	2	100° C	3,1147

The plan of the experiments and the results ensuing from them are given in Table 9.

Table 9. Plan of the full factor experiment

	Parameters							
N°	X_1, %	X_2, g	X_3, h	X_4, °C	X_5, g	Y, g	$\hat{Y}$ g	Residues
1.	15	8,1027	3	90	8,4585	1,6570	1,8382	-0,1812
2.	15	13,4993	3	90	2,3028	1,9037	2,0848	-0,1811
3.	25	8,1031	3	90	8,4645	1,6300	1,2008	0,4293
4.	25	13,5044	3	90	2,2518	0,7830	1,5482	-0,7652
5.	15	8,1038	7	90	8,4614	3,7586	3,3727	0,3859
6,	15	13,5083	7	90	2,2591	3,7818	3,6948	0,0869
7.	25	8,0985	7	90	8,4613	3,2845	2,7596	0,5249
8.	25	13,5035	7	90	2,2561	2,7704	3,0843	-0,3139
9.	15	8,1099	3	110	8,4677	4,9114	5,0901	-0,1787
10.	15	13,5015	3	110	2,2581	5,9740	5,4527	0,5214
11.	25	8,1110	3	110	8,5693	4,6083	4,2648	0,3435
12.	25	13,5104	3	110	2,2586	4,8051	4,8047	-0,0023
13.	15	8,1055	7	110	8,4624	5,6982	6,6526	-0,9544
14.	15	13,5036	7	110	2,2503	7,4926	7,0058	0,4868
15.	25	8,1013	7	110	8,4643	5,6488	6,0332	-0,3844
16.	25	13,4989	7	110	2,2544	6,5369	6,3832	0,1537
17.	20	10,8008	5	100	4,5022	5,8051	5,7764	0,0287

We have found the coefficients b_i, i = 0,1,2,...5 from Eq. (3) according to the method of the least squares, using a program for finding an equation of a multiple linear regression (System/360 1970). The results are presented in Table 10.

where:

free term $b_o = 20.9779$

coefficient of multiple correlation

$R_{mtpl} = 0.9741$

The multiple coefficient of correlation is a measure of the linear dependence between $\hat{y}$ and the set of variables X_1, X_2, X_3, X_4, X_5 as $O \leq R_{mtpl} \leq 1/15/$. This shows that there exists a strong linear dependence of the yield $\hat{y}$ on the factors $X_1 \ldots\ldots X_5$.

The equation adequately describing the experimental data is:

$$\hat{y} = 20.9779 - 0.0625X_1 - 2.1784X_2 + 0.3856X_3 + 0.1643X_4 - 1.9499X_5$$

It is evident from the equation obtained that the influence of the initial amounts of glucose and glycine is the strongest. The maximum yield was obtained at a close ratio of the reaction components. The influence of temperature and time is weaker while that of water is the weakest.

We have further investigated the optimum value of the yield within the range of variables studied using the simplex method (Božanov 1973). The optimum values of the yield and the parameters X are:

$\hat{y}_{max} = 7.6178$ g
$X_{1_{max}} = 15\%$
$X_{2_{max}} = 12.1500$ g
$X_{3_{max}} = 7$ h
$X_{4_{max}} = 110\,°C$
$X_{5_{max}} = 3.4500$ g

Taking into consideration everything presented so far, we have drawn the conclusion that the optimum conditions of obtaining nondialyzable melanoidines are as follows: the ratio - glucose:glycine = 1:0.68M; temperature 110 °C; reaction time 7 h; water content 15%. We have confirmed experimentally the quantitative inferences for the maximum yield at optimum reaction conditions. At the optimum parameter values, thus established, we have performed an experiment and obtained 7.7393 g, at $\hat{y}_{max} = 7.6178$.

Table 10. Elements of multiple regression

Factors	Mean value	Standard deviation	Correlation coefficient X/Y	Regression coefficient	Standard error of regression coefficient	T -Value estimated
X_1	20,000	5,000	-0,16402	-0,0625	0,02658	-2,3509
X_2	10,8039	2,6996	0,0916	-2,1784	0,7209	-3,0219
X_3	5,000	2,000	0,4076	0,3856	0,0665	5,7957
X_4	100,00	10,000	0,8379	0,1643	0,0133	12,3582
X_5	5,3178	3,1147	-0,1061	-1,9499	0,6248	-3,1206

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LENGTHENING THE POSTHARVEST LIFE OF PEACHES BY COATING WITH HYDROPHOBIC EMULSIONS

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ABSTRACT

In this study peaches were coated with three different hydrophobic emulsions and stored at room conditions (21–24°C and 57–63% R.H). The decrease in weight and the changes in the total titratable acidity, ascorbic acid and soluble solids contents, pH and the organoleptic characteristics of the coated and uncoated (control) samples were determined periodically.

The rate of the weight decrease and the changes in the chemical structure and texture of the peaches were lower with the beeswax-coconut oil emulsion coated peaches than the uncoated peaches. While the maximum acceptable shelf-life for uncoated samples was 10 days, the samples coated with this emulsion maintained their acceptability for 14 days.

The coating of the peach surfaces with this emulsion decreased the water vapor and oxygen gas transfer, resulting in the diminished respiration rate thus increased the shelf-life of the fruit.

INTRODUCTION

The fruits and vegetables continue to respire after harvest. The oxygen consumed from the air reacts with glucose to give carbon dioxide and water. This reaction represents a host of complex reactions responsible for postharvest ripening and aging. Exposure to ordinary atmospheres promotes dessication or water loss which detracts from fresh quality and also promotes bacterial and fungal deterioration.

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The optimum extension of the postharvest life of food products is critically dependent upon three factors (1) reduction in dessication, (2) reduction in the physiological process of maturation and senescence and (3) reduction in the onset and rate of microbial growth. Unless all three factors are carefully controlled optimum extension of postharvest life is not achieved.

An important approach to minimize or eliminate these problems is to coat the individual fruits and vegetables and in effect provide a protective film for prolonged freshness. If the coating is water-soluble, it can be removed by simple washing by the consumer, if it is not water-soluble, it can be removed by peeling the fruit's skin.

Some hydrophobic substances such as beeswax or paraffin wax and some polymers have been used as coating materials. Cothran (1955), used wax compositions for citrus fruits, Scott and Greenley (1959) used vinylidene-acrylonitrile copolymer, Durst (1967) used natural materials such as vegetable oil emulsion and melted lard emulsions to coat fig bar, Rosenfield (1968) used vinyl acetate, 2-ethylhexyl acrylate copolymer to coat cantaloupes, Ukai *et al.* (1976) used hydrophobic emulsions to coat fruits and vegetables such as orange, peas, apples, green beans, tomatoes, pears, peaches. Cunning and Caulkins (1965), Glasgow and Kraght (1970) developed apparatus for coating fruits. Tal-Chemicals Company produced a coating composition "Tal-Prolong" consisting of sucrose esters of fatty acids, carboxymethylcellulose sodium salt, mono and diglycerides of fatty acids (all of them FDA approved chemicals) to lengthen the fruit shelf-life. However, this product gave disappointing results on English plums (Browning 1982). Erbil and Teoman (1985) used polymer-wax emulsions to coat the rapidly deteriorating fruits such as cherries, morello cherries, grapes, peaches, pears and satsumas.

It was determined that when a film of very low oxygen permeability is formed to coat the fruit and the minimum quantity of oxygen required for respiration cannot be absorbed in, alcohol is produced as a result of anaerobic fermentation, instead of carbon dioxide and water. Additionally it is nearly impossible to find a single water soluble polymer with good water vapor barrier character because in a water soluble film the solubility of water-vapor molecules is high, resulting in high water-vapor permeability. The solution is the production of a heterogeneous film consisting of hydrophobic particles within a hydrophilic matrix. The hydrophobic emulsion thus coats the fruit surface and dries to form a coating membrane which comprises fine continuos microvoids being formed between the hydrophobic microparticels and the matrix polymer. It has been found that if the quantity of the water-soluble polymer is excessive relative to the quantity of hydrophobic microparticles, the water-soluble polymer surrounds the microparticles and the continuous microvoids that allow the transfer of gas molecules cannot be formed. On the other hand if the quantity of the water soluble polymer is too little, the formability of the continuous membrane becomes

poor. The particle size is also important, it should be between 1–5 microns in diameter. It is also found that a coating that is suitable for one fruit is not necessarily suitable for another fruit due to the skin structure and oxygen demand differences. The determination of the most appropriate coating for every kind of fruit should be investigated separately.

The purpose of this research was to investigate the effect of three emulsion coating compositions on some chemical parameters, organoleptic characteristics and the dessication rate of the coated peaches in comparison with the uncoated peaches.

MATERIALS AND METHODS

The peaches (Halley variety) used in the experiment were obtained from the orchard of a local agricultural high school. The fruits were carefully selected to insure uniformity in maturity, size and color. Peaches were divided into four replicate lots. First lot consisted of control samples stored without being coated. Lots 2–4 were coated with three different emulsions. The compositions of the emulsions are given below:

The Preparation of Emulsions

A-100 parts paraffin wax and 20 parts emulsifier EMULGIN PE (Turk-Henkel Co.) were mixed at 70 °C. 2.5 parts carboxymethyl-cellulose sodium salt (MERCK) were dissolved in 500 parts water at 70 °C. The hot wax mixture was added to aqueous solution at 70 °C in a reactor equipped with a stirrer at 1300 rpm in 10 min. The stirring continued for 1 h more, then left to cool.

B- 125 parts beexwax, 20 parts triethanolamine (MERCK) and 16 parts oleic acid (technical) were mixed at 70 °C. The hot mixture was added to 500 mL water at 70 °C with same conditions as sample (A).

C- 25 parts beeswax, 25 parts coconut oil (technical) were mixed at 70 °C. Four parts sodium oleate (Riedel-de Haen) were dissolved in 500 mL water at 70 °C and the hot wax mixture was added with same conditions as sample (A).

Coating of the Peaches

Each lot of peaches was placed separately into an open container with a wire mesh bottom, in a single layer. The prepared emulsions were sprayed on the surface of the samples using a spray pistol at 40 °C. During spraying, the peaches were carefully rolled over in order to provide a uniform coating on the surface. The film formed on the surfaces was dried by blowing air for 5 min.

Analytical Methods

Three lots of coated peaches and control samples were stored at room conditions (21–24 °C and 57–63% R.H.).

The following analyses were carried out to examine the quality changes of the samples:

(1) Weight loss: The weight loss occured due to transfer of water vapor from the samples to air was determined by weighing the samples immediately after coating and then every day with a digital balance (METTLER PE 3600) and was reported as percent loss by weight.

(2) Titratable acidity: The method described by Lees (1971) was used in the determination of titratable acidity.

(3) pH: 50 g samples were blended with 150 mL distilled water and pH was measured with a pH meter (KENT EIL 7045/46).

(4) Ascorbic acid: Ascorbic acid was assayed using 2.4 dichlorophenolindophenol spectrophotometric method of Pearson (1976).

(5) Soluble solids: Soluble solids in the peach juice were measured with a temperature controlled refractometer and were reported as percent by weight.

(6) Sensory evaluation: A trained panel consisting of 5–7 members evaluated the appearance, color, texture and flavor of the samples throughout the storage period. The samples were randomized and were served on similar plates on a table specially illuminated to carry out sensoric tests. For overall acceptability a nine point hedonic scale was used (1 = extremely undesirable and 9 = extremely desirable). The panelists were requested to rate two replications of each sample group on an evaluation sheet. Sensory evaluation was reported as the average of the scores of the panel members.

RESULTS AND DISCUSSION

According to the results of the control sample analyses, 100 g of peaches contained 14.27 g total solids, 12.90 g soluble solids, 0.43 g titratable acid, 10.40 mg ascorbic acid and the pH was 3.48 at the beginning of the storage period.

The weight percent of the films formed on the surface of the samples after coating with emulsions, A, B and C was found to be 1.04, 1.20 and 0.94%, respectively.

The weight loss and the changes in the titratable acidity, ascorbic acid, soluble solids, pH and organoleptic characteristics of the coated and uncoated (control) samples are shown in Fig. 1–5. The analyses were carried out until the overall acceptability was below 5 points for each lot of samples.

Figure 1 shows the increase in weight loss as storage time increases. Average daily weight losses in the samples coated with emulsions (A), (B), (C) and uncoated samples were 2.74, 0.76, 1.40 and 1.75%, respectively.

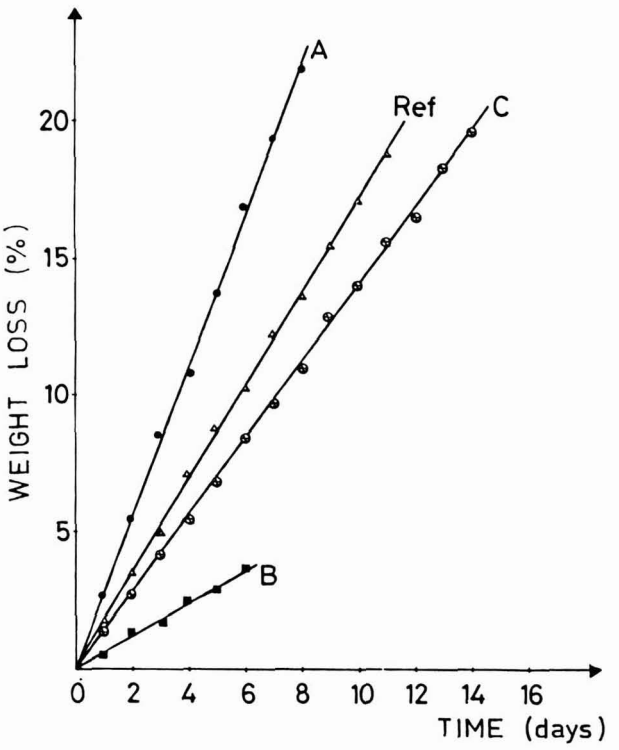

FIG. 1.
THE INCREASE OF THE WEIGHT LOSS OF PEACHES WITH TIME

The samples coated with emulsion (B) showed the greatest decrease in titratable acidity whereas the decrease was lowest in the samples coated with emulsion (C) as seen in Fig. 2. The acid degradation is related to the respiration rate (Vandercook 1977).

Figure 3 shows the increase of the pH values of the samples reflecting the decrease in titratable acidity.

As shown in Fig. 4, the rate of ascorbic acid loss was higher in the control samples than the samples coated with emulsion (C) over the entire storage period. However the ascorbic acid content of the samples coated with emulsions (A) and (B) decreased more rapidly than the control samples. The rapid decrease in ascorbic acid content was due to the increased oxygen uptake at higher respiration rates.

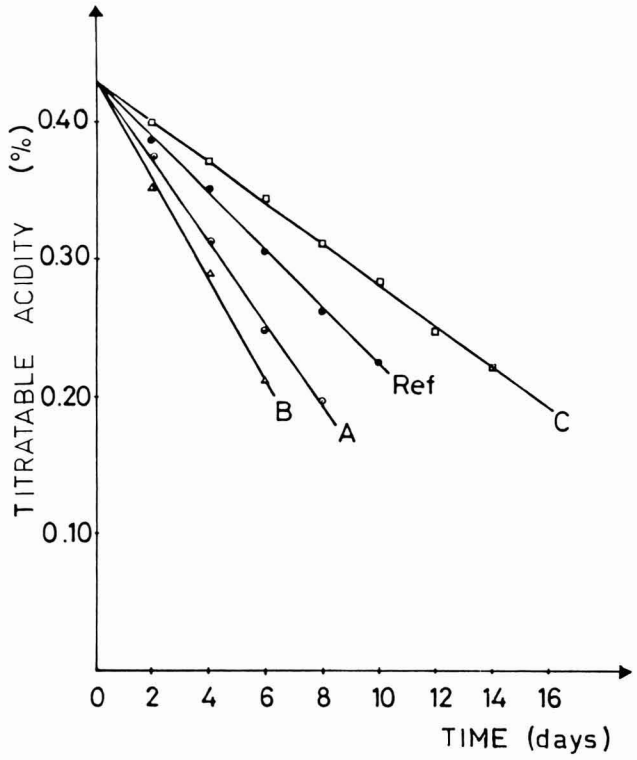

FIG. 2.
THE DECREASE OF THE TITRATABLE ACIDITY OF THE PEACHES WITH TIME

The order of the decrease in the total soluble solids of the samples was similar to the decrease in the ascorbic acid contents of the samples as shown in Fig. 5. The decrease in the soluble solids content was mainly due to the reduction in carbohydrate content of fruits during respiration.

As can be seen in Fig. 6, the samples coated with emulsion (C) received the highest mean hedonic scores for overall acceptability throughout the study. However, the organoleptic properties of the samples coated with emulsions (A) and (B) decreased rapidly to the unacceptable level after a storage period of one week.

A bright film was formed on the surface of the peaches after coating with emulsions (A) and (C) and the film could be easily removed by washing with water. However, coating with emulsion (B) resulted in a dull film which was hardly dissolved in water. Samples coated with emulsions (A) and (B) were found to be suitable medium for mold growth on the surface after one week storage.

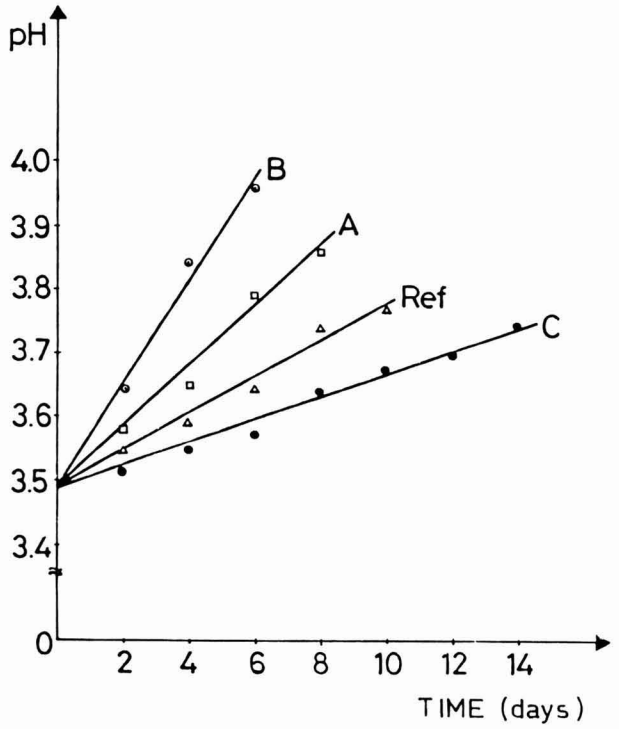

FIG. 3.
THE INCREASE OF THE pH VALUES OF THE PEACH JUICES WITH TIME

The analytical results showed that the samples coated with emulsions (A) and (B) had higher respiration rates than control samples. Carboxymethylcellulose sodium salt which was a component of emulsion (A) caused higher oxygen and water vapor transfer than was expected. Emulsion (B) containing high amounts of beeswax resulted in the lowest water vapor transfer, however did not decrease the oxygen transfer rate appreciably due to the heterogeneous film formation containing large microparticles. Since the size of the microchannels formed between these large microparticles was also large, the coating could not prevent the transport of oxygen and carbon dioxide molecules sufficiently.

The coating of peach samples with emulsion (C) reduced the water vapor and oxygen transfer rates and lengthened the postharvest life of the fruit. No mold growth was recognized on the surface after two weeks storage. The reason for the suitability of this coating was the formation of a layer having small microparticles containing beeswax and coconut oil. Since the size of the microchannels

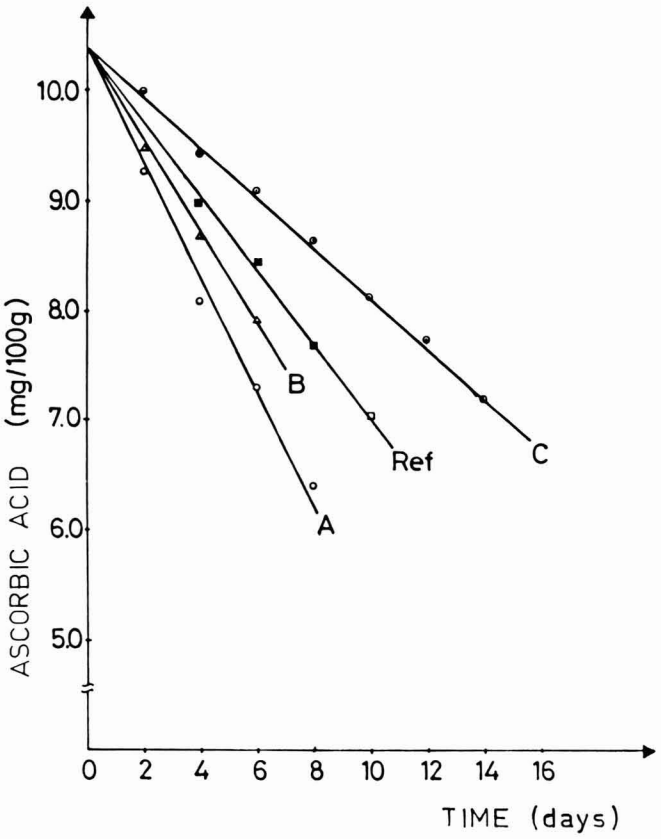

FIG. 4.
THE DECREASE OF THE ASCORBIC ACID CONTENT OF THE PEACHES WITH TIME

between these small microparticles was also small, the coating decreased the oxygen and carbon dioxide gas transfer and thus respiration rate. However, the peaches could absorb more oxygen than the minimum quantity required for respiration and anaerobic fermentation did not take place.

The experiments exhibited the effect of the size, nature and the amount of the hydrophobic microparticles on the respiration and dessication rates. Since the size of the microparticles depended on the nature of the hydrophobic ingredient, their weight ratio in the emulsion composition and the stirrer rate, these parameters should be carefully selected in order to obtain better control on water vapor, oxygen and carbon dioxide transfer rates of the coating.

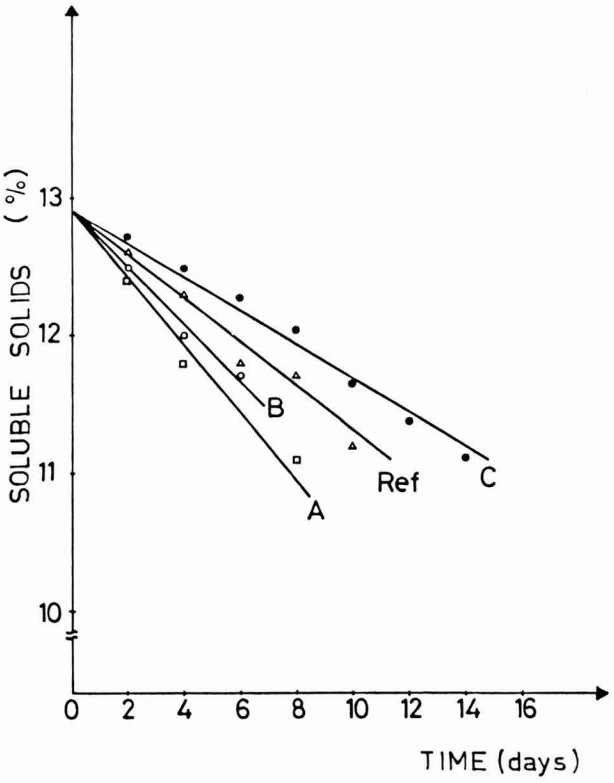

FIG. 5.
THE DECREASE OF THE SOLUBLE SOLIDS PERCENT OF THE PEACHES WITH TIME

CONCLUSIONS AND SUGGESTIONS

The coating of the peach samples with some hydrophobic emulsions effected the rate of changes in some chemical and organoleptic properties of the fruits during room temperature storage. Coating with emulsions (A) and (B) was not effective in lengthening the shelf-life of the fruits. However, coating with emulsion (C) slowed down the rate of deterioration and lengthened the shelf-life. While the maximum acceptable storage period for uncoated samples was 10 days, the samples coated with emulsion (C) maintained their acceptability for 14 days.

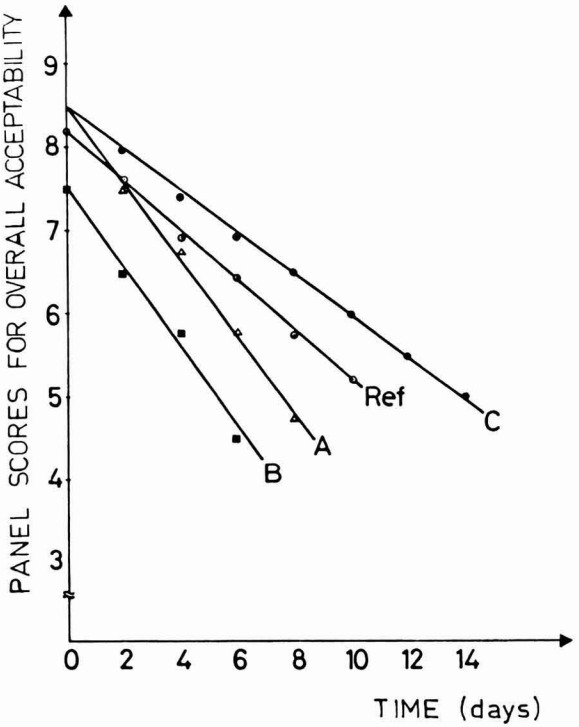

FIG. 6.
THE DECREASE OF THE PANEL SCORES FOR OVERALL ACCEPTABILITY OF PEACHES WITH TIME

It is well known that some fruits are harvested when they are not ripe and ripening continues after harvesting. The respiration rate is high at the beginning of the ripening and decreases as the maturity proceeds (climacteric characteristics). The peaches used in these experiments were coated with the emulsions when they were at eating maturity. Coating of the peaches with emulsion (C) and some other similar hydrophobic compositions just after harvesting would definitely be more effective in legthening the postharvest life.

In the light of these conclusions further studies covering the preparation of suitable hydrophobic emulsions and coating peach and other more perishable fruits is suggested.

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THE EFFECT OF STORAGE TEMPERATURE ON QUALITY OF CITRUS PRODUCTS ASEPTICALLY PACKED INTO STEEL DRUMS

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ABSTRACT

Orange and grapefruit concentrate (60°Bx) and orange drink base were filled aseptically into 210 l drums without any effect on product quality. Orange products could be stored at 2°C for about 18 months with little effect on their quality. However, grapefruit concentrate could not be held longer than 6–7 months at 2°C. Nonrefrigerated shipment of aseptically filled orange concentrates and bases is permissible except under hot summer temperatures. Grapefruit concentrates, however, should not be exposed to temperatures about 15°C for more than a few days. Product deterioration can be followed by measuring degree of browning, and shelf-life can be predicted approximately, using this parameter and its reaction rates at various temperatures. Thus, this method of preservation can give considerable savings in processing, storage, and transportation costs. However, in order to insure maintenance of product quality, precautions must be taken as regards exposure to elevated temperatures (above 15°C) for extended periods.

INTRODUCTION

Citrus products intended for industrial reprocessing are usually stored and transported in a frozen or semi-frozen state (i.e., at −10°C to −20°C) or preserved chemically and kept at ambient or refrigerated temperatures. Forms of storage and transport vary and include 200 liter drums or bulk (tank farms) storage and bulk transport for the frozen products, or 200 liter to 2000 liter plastic containers for the chemically preserved products.

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Quality is best maintained in the frozen state but storage and transport costs are high. Chemical preservation is losing in importance due to market resistance to chemical additives. This method is essentially limited to citrus bases intended for the soft drink market.

Aseptic packaging of thermally processed juices and fruit drinks, in 1 to 4 liter containers in general and citrus products in particular, is commercially well established worldwide (Carlson 1984). The most successful application of aseptic techniques for products in larger containers has been the packaging of tomato products in 55 gallon drums and larger (Nelson 1984).

Citrus products, such as concentrates and bases, also lend themselves easily for existing aseptic filling systems with respect to microbial stability. However, these products are prone to rapid chemical deterioration which is highly dependent on storage temperature. Of particular importance are nonenzymatic browning reactions, loss of ascorbic acid and onset of off flavors often characterized as cooked taste.

There is no published information regarding the stability of these products aspectically filled into large containers, such as drums, and stored at ambient temperatures. The object of this work was to determine the effect of storage temperature and temperature fluctuation on quality of citrus products aseptically packed into steel drums.

MATERIALS AND METHODS

Citrus Products

Commercial frozen Shamuti orange (OCB) and Marsh Seedless grapefruit (GCS) juice concentrates (60 °Bx) as well as a commercial frozen orange drink base (OB) were used. The base had a total soluble solid concentration of 30 °Bx and consisted of a mixture of orange concentrate, pump, comminuted fruit, orange oil and colorant. The concentrates had been manufactured by extracting fruit on FMC INLINE extractors, screening, pasteurizing and concentrating in a "TASTE" tubular evaporator, slush freezing in a swept surface heat exchanger and storing in 200 liter drums at −20 °C until use.

Packaging Materials

A. 210 and 55 liter steel drums internally lined with plastic films (supplied by Van Leer B.V., Amstelveen, Netherlands) were used in the storage study. Drums were supplied with 5 in. gasketed caps which were sealed onto the drums (after filling) by means of a special pneumatic closing machine.

B. 350 mL glass jars with 58 mm "white cap" twist-off closures were used for the kinetics studies.

Analytical Methods

Total soluble solids (°Bx) were determined using a Baush and Lomb Abbe refractometer with reading accuracy of ±0.25 °Bx.

Acidity was determined by titration with 0.3 N NaOH and expressed as percent anhydrous citric acid.

Hydroxymethyl furfural (HMF) was measured according to Keeney *et al.* (1959). The products were diluted to 11 °Bx, clarified with lead acetate, filtered, reacted with thiobarbituric acid and read at 443μ in a Baush & Lomb Spectronic 20 Spectrophotometer. Results are given in ppm HMF.

For browning, the diluted (11 °Bx) sample was clarified with lead acetate, filtered, and optical density was read at 420μ in a Spectronic 20 Spectrophotometer. The optical density (OD) so determined is the "Browning Index" of the sample.

Ascorbic acid (AA) was determined by 2,6 dichlorophenol indophenol titration and expressed as mg per 100 g product (AOAC 1970).

d-limonene concentration was obtained by bromide-bromate titration and given as mg/kg (Scott and Veldhuis, 1965).

Cloud stability of 11 °Bx samples was evaluated by checking separation in a 100 mL graudated cylinder, at room temperature, after ½ h and 2 h.

Sensory evaluations of 11 °Bx products were carried out by a trained panel. Orange base was tasted in a drink made from one part base and nine parts 10% sucrose solution with 0.2% citric acid. Initially, taste evaluations were made using the triangle test. After differences were found between control stored at −40 °C, and test samples, hedonic rating evaluations were carried out using a scale of 1 to 5 with: 5 very good, 4 good, 3 fair, 2 poor, 1 very poor.

Tasters were also asked to comment on objectionable taste characteristics.

Microbial evaluations were made on products before processing and after aseptic filling into drums and jars. Products were evaluated for spoilage organism count (SOC) and fermentation (Weissman 1975).

Sample Preparation and Packaging

The products were thawed at room temperature, pumped through a swept surface heat exchanger (Schroder, Germany), heated to 85° ± 1 °C for 15 s, and cooled in a second swept surface heat exchanger to 18–25 °C by means of ice water. The sterile product was filled into presterilized drums or jars under a laminar flow hood, through a specially fitted filling cap. The filling cap comprised a product inlet, an air outlet equipped with a glass wool packed filter, a steam inlet and a sight glass. Drums were presterilized with hot water and live steam. The jars were presterilized in an autoclave at 110° for 30 min with the lids loosely screwed on. Filled containers were immediately sealed, rinsed, and stored at 4 °C before distribution to various storage conditions.

Storage

Products in jars were held at 6 constant temperatures: −18°, 2°, 10°, 15°, 25° and 35 °C. This was done in order to obtain kinetic data on the deleterious reactions in these products for shelf-life prediction of products in drums, based on their time/temperature histories.

The drums were stored at +2 °C. Some of the drums were subjected to variable time-temperature patterns simulating transport and static conditions as shown in Table 1.

Table 1. Storage pattern of steel drum with citrus products

		Storage Pattern (1)		
		A	B	C
Simulated Action	Duration	Temperature °C		
Pre-shipment storage	3-5 months	2	2	2
Inland Transport	7 days	25	15	15
Ship Loading	10 days	25	15	15
Ships Voyage	5 days	35	25	15
Unloading & Inland Transport	7 days	25	15	10
Storage	12 months	2	2	2

(1) Patterns A, B and C represent shipment conditions in hot (summer) warm (spring and fall) and cool (winter) weather, respectively.

RESULTS AND DISCUSSION

Adequacy of the Aseptic Filling Procedure

The characteristics of the starting material, after processing, filling and sealing are given in Table 2. Microbial evaluation of raw material prior to processing gave 100 to 300 counts/g of spoilage organisms and a positive fermentation test, while aseptically filled products showed less than 10 counts/g and a negative fermentation test. None of the drums showed any signs of fermentation during the entire trial. After 18 months or more of storage, none of the drums showed any signs of visual damage to the internal coating regardless of product or storage conditions. It may be concluded that the aseptic filling procedure was technically adequate and did not, in itself, affect the quality of the products appreciably.

Table 2. Some characteristics of citrus products

Product	°Brix	Acidity (%)	Browning (OD at 420 nm)	HMF ppm	Ascorbic Acid mg/100 g	d-limonene mg/kg	Cloud Stability 2 hr	Sensory Characterization	Score
Orange Conc. (OCS)	60.6	6.13	0.14	14	206	47	stable	Sour, pale color	5*
Grapefruit Conc. (GCS)	59.0	7.40	0.23	14	194	90	stable	Good taste, slightly brown	5*
Orange Base (OB)	30.2	6.26	0.19	180	92	510	stable	Good taste & color	5*

*No difference between frozen blank and this sample

Storage Temperature and Shelf-Life

The effect of temperature on some quality parameters of OCS, GCS, and OB stored in glass jars at fixed temperatures are given in Tables 3, 4, and 5. These results show that browning and taste scores were more consistent indicators for quality changes than hydroxy-methyl furfural and ascorbic acid degradation. Based on the above results, and taking a score of 3 as end of storage life, the conclusions regarding shelf-life are summarized in Table 6.

Table 3. Effect of temperature on aseptically filled orange concentrate in glass jars (OCS)

Temperature (°C)	Time (Weeks)	Browning (O.D)	HMF (ppm)	Ascorbic Acid mg/100g	Taste[1] Score
10	1	0.14	12	190	5*
	12	0.14	16	190	5*
	24	0.15	10	185	5*
	46	0.15	16	157	5*
15	1	0.14	12	190	5
	12	0.14	12	190	5
	24	0.16	12	158	4.8
	46	0.19	16	146	3.3
25	1	0.14	12	190	5*
	8	0.15	19	190	3.7
	16	0.22	28	141	2.0
	20	0.26	41	138	1.5
	24	0.29	60	116	1.0
35	1	0.14	14	190	5*
	2	0.17	24	190	4.0
	3	0.18	34	180	2.0
	4	0.19	38	150	1.0
	8	0.25	72	180	—

1) 5* Identical to frozen produce (blank)
5 Very good but different from blank
4 Good
3 Fair
2 Poor
1 Very Poor

Table 4. Effect of temperature on aseptically filled grapefruit concentrate in glass jars (GCS)

Temperature (°C)	Time (Weeks)	Browning (O.D)	HMF (ppm)	Ascorbic Acid mg/100g	Taste[1] Score
10	1	0.21	16	196	5*
	12	0.25	13	196	4
	16	0.28	10	-	3.1
	20	0.29	12	-	2.0
	24	0.30	13	170	1
15	1	0.21	16	196	5*
	8	0.26	14	194	4.0
	12	0.30	14	194	2.0
	16	0.35	13	185	1.0
25	1	0.22	16	194	5.0
	4	0.32	16	194	1.0
	12	0.39	30	187	—
35	1	0.31	21	196	3
	2	0.35	25	170	1

[1]See remarks Table 3

Table 5. Effect of temperature on aseptically filled orange drink base in glass jars (OB)

Temperature (°C)	Time (Weeks)	Browning (O.D)	Ascorbic Acid mg/100g	Taste[1] Score
10	1	0.16	95	5*
	12	0.21	85	5.0
	24	0.26	67	4.6
	46	0.33	50	3.4
15	1	0.16	90	5*
	12	0.23	85	5.0
	24	0.28	67	4.2
	46	0.42	46	2.7
25	1	0.19	87	5*
	8	0.26	79	4.0
	16	-	62	3.0
	24	-	55	2.0
35	1	0.16	95	5*
	2	0.20	82	4.7
	4	0.26	78	3.3
	8	0.33	73	2.0

[1]See remarks Table 3

Table 6. Shelf-life of citrus products at different temperatures

Product	Temperature (°)	Shelf Life[1] (Weeks)
OCS	10	46
	15	46
	25	10
	35	2.5
GCS	10	16
	15	10
	25	2-3
	35	1
OB	10	46
	15	30-40
	25	16
	35	6

[1]Approximate time to reach taste score of 3

The effect of storage at 2 °C for 18 months on some quality parameters of the products packaged in 55 liter plastic lined steel drums is shown in Table 7. Both orange products kept extremely well, with almost no browning or taste deterioration. Grapefruit concentrate underwent some browning and taste deterioration but was still acceptable at the end of the 18-month storage.

Table 7. Effect of 18 months storage at 2 °C on citrus products in 55 liter steel drums

Product	Storage Time (months)	Browning (OD)	HMF (ppm)	Ascorbic (mg/100g)	Taste Score (1)
OCS	0	0.140	14	190	5*
	18	0.135	14	185	5*
GCS	0	0.210	14	196	5*
	18	0.295	16	180	3.5
OB	0	0.160	180	95	5*
	18	0.200	300	62	4.5

(1) See remarks Table 3

The results of shipment simulation of the three citrus products are given in Table 8. These data show that the "summer" (Pattern A) simulation was very severe and only the orange base (OB) still remained acceptable with a good color and taste at the end of shipment. The intermediate climate simulation (Pattern B) also rendered the grapefruit concentrate totally unaccpetable in taste and appearance at the end of the trial. The other two products remained in a very good state. Only the cool climate simulation (Pattern C) left the orange products in very good quality, and the grapefruit concentrate in good (acceptable) quality.

Kinetics of Browning

The rates of browning for orange concentrate, grapefruit concentrate and orange base are shown in Fig. 1, 2, and 3, respectively. The straight lines were drawn assuming zero order kinetics (Labuza 1981) and submitting the experimental points to linear regression analysis. The slope of these curves is the rate constant k in the integrated form of the zero order reaction rate equation:

$$B = B_o + kt \qquad (1)$$

where

B = Browning index at time t

B_o = Initial browning index

Table 8. Browning values and taste scores of citrus products in drums at end of shipment simulation

Simulation Pattern	A		B		C	
Product	Browning OD	Taste Score	Browning OD	Taste Score	Browning OD	Taste Score
OCS	0.16 (0.14)	2.3	0.16 (0.16)	4.3	0.16 (0.16)	5
GCS	0.32 (0.22)	1.0	0.28 (0.22)	1.0	0.30 (0.22)	3.8
OB	0.23 (0.16)	3.8	0.20 (0.16)	4.7	0.16 (0.16)	5

Note: Figures in brackets give values at start of simulation

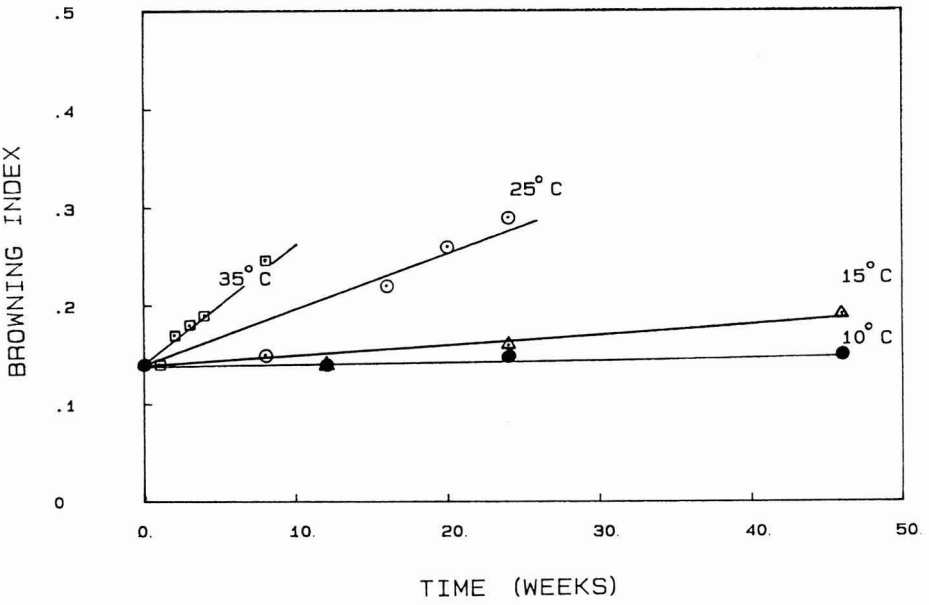

FIG. 1.
RATE OF BROWNING OF ORANGE CONCENTRATE (OCS)

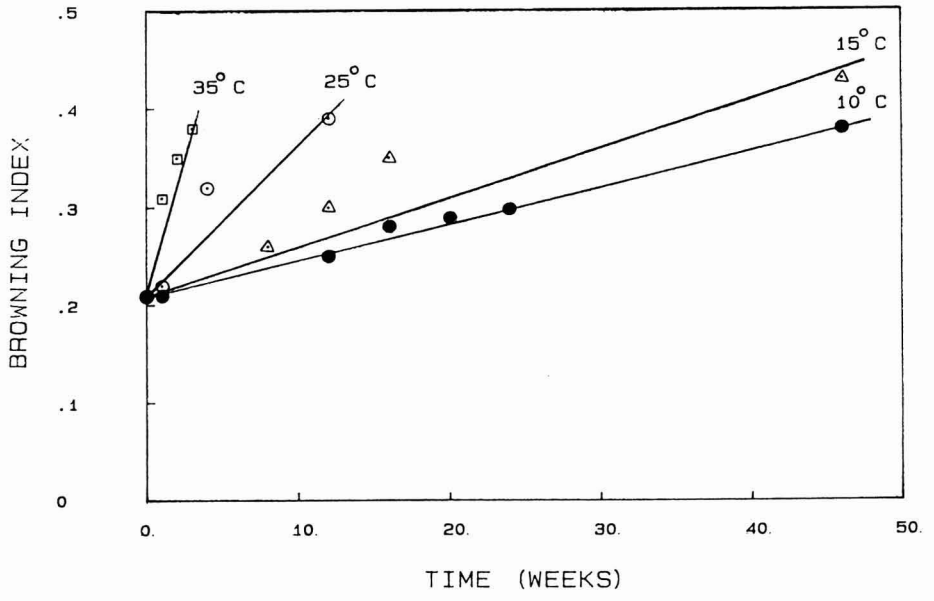

FIG. 2.
RATE OF BROWNING OF GRAPEFRUIT CONCENTRATE (GCS)

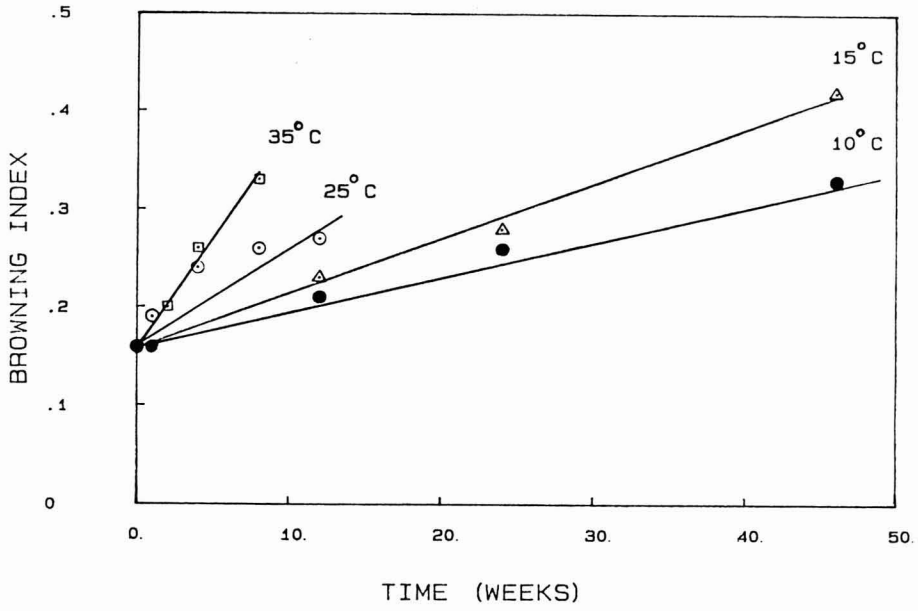

FIG. 3.
RATE OF BROWNING OF ORANGE BASE (BO)

Table 9 lists the rate constants and the linear regression coefficients for the three products, at different temperatures.

The dependence of k on temperature is found to obey quite well an Arrhenius type relationship:

$$\log k = A - E/RT$$

where
E = energy of activation
T = absolute temperature
A,R = constants

The regression coefficients for the linearity of log k with 1/T and the energies of activation as calculated from the slope of the lines are given in Table 10. These data, together with information on expected time-temperature profiles, provide a useful basis for the prediction of quality loss and shelf-life of the products investigated, under given conditions of storage.

Table 9. Slopes and regression coefficients for browning vs. time curves for three citrus products at different temperatures

Product	Temp. °C	Slope (rate constant k) (1/week)x10^4	Linear regression coefficient R
OCS	10	2.5	0.879
"	15	11.1	0.967
"	25	63.9	0.972
"	35	140	0.962
GCS	10	37.6	0.996
"	15	48.3	0.952
"	25	150	0.953
"	35	550	0.958
OB	10	37.7	0.994
"	15	56.3	0.996
"	25	87.0	0.921
"	35	227	0.986

Table 10. Energies of activation and linear regression coefficients for arrhenius' equation for browning in three citrus products

Product	Activation Energy E Cal/mol.	Linear Regression coeff. R
OCS	27600	0.975
GCS	19100	0.990
OB	12000	0.984

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INFLUENCE OF BRINING PROCEDURES ON SALT CONTENT AND DISTRIBUTION IN SMOKED WHITEFISH CHUBS

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ABSTRACT

In order to determine processing parameters, commercially smoked chub were analyzed for salt and moisture and for visual quality by trained judges using industry criteria. Desirable smoked chub from both convection and controlled environment smokehouses contained approximately 3.2% water phase salt (SWP) while those of lower quality were higher in SWP and lower in moisture. Conventional brining studies on chub yielded center sections of dorsal muscles with lower SWP than either end of the muscle. External and internal areas of dorsal muscles analyzed after brining and hanging for 14 h were similar in SWP within brines and times in brine. Chub (63-134g) brined in experiments with 6.6% NaCl brine for 16 h and leached in 2% NaCl solution for 24 h were more uniform in SWP after smoking than chub leached in 3.3% (38°F) water for 20 min. Modifications in brine concentration and/or time in brine may be necessary for larger chub.

INTRODUCTION

Conventional processing of smoked whitefish chub includes a brining treatment followed by smoking, usually at low temperatures. A survey of processes employed by the smoked fish industry (Kautter 1964) showed that variation in brine concentration ranged from 18–100 degrees salometer (4.75–26.4% salt) and that time in brine ranged from 1–48 h, depending upon the size and type of fish and whether they had been frozen prior to processing. Smoking temperature ranged from 30 °C (86 °F) to 87.8 °C (190 °F) for 0.25–8.0 h. Both brining and smoking time differences were based on the general experience and "know how" of the personnel and not on scientifically controlled procedures. Weckel and

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Wosje (1966) confirmed that smoked chub processors used a wide range of salt (5–15%) in their brines and variable time periods for brining. In addition, their survey revealed variations in temperatures of brine, in the size of chub in one tank, and in the degree of circulation of brine about the chub during brining. A study by these workers showed that all of the above factors as well as scaling influenced the rate of salt absorption from brine.

Variations in commercial processes for smoked chub are reflected in moisture and salt contents of the finished products. In 7 smoked chub samples collected by FDA inspectors (Kautter 1964), moisture ranged from 61.19 to 72.65% while sodium chloride levels ranged from 1.56 to 4.30%. Low moisture generally coincided with low salt content and high moisture with high salt content. Weckel and Wosje (1966) reported that salt uptake in the loin muscle varied as much as 200% among fish brined in the same tank. Christiansen *et al.* (1968) reported a range of 1–3.5% brine in the contralateral loin (dorsal) muscle of medium sized chub brined in either 7.9% NaCl for 4 h or 11.9% NaCl for 8 or 20 h.

The variation of water phase salt (SWP) among and within chub limits the value of sodium chloride as a preservative and particularly as an agent to inhibit growth and toxin production of type E *Clostridium botulinum*. Christiansen *et al.* (1986) reported that at least 3% SWP in the smoked product is necessary to inhibit spore outgrowth and toxin production. Also, they found that conventional brining techniques resulted in excessive salt in the thinner sections of the fish when 3% SWP was attained in the loin muscle. This nonuniformity of salt distribution resulted in a commercially unacceptable product.

Since *Clostridium botulinum* type E is found in fish from the Great Lakes (Bott *et al.* 1966; Pace *et al.* 1967; Sugiyama *et al.* 1972) and the potential botulism hazard has been demonstrated by the outbreaks of 1960 (Anonymous 1960) and 1963 (Kautter 1964), the proper use of sodium chloride and other processing parameters that results in effective microbiological control, safety, and consumer acceptance is important. Kosak and Toledo (1981) developed a two-stage brining procedure for mullet that resulted in minimal differences in SWP between the thick and thin sections of a fish. The purpose of this study was to adapt the two-stage brining procedure to whitefish chub in order to reduce variation of salt ($>$3.0%) in the water phase after processing between thick (dorsal) and thin (ventral) sections of the fish.

MATERIALS AND METHODS

Characterization of Commercially Produced Smoked Chub

Physical and chemical quality characteristics of New York area commercially smoked chub were determined. Thirty-nine smoked chub from a New York City

processor's regular packaging line were measured for physical dimensions and subjectively rated by two researchers experienced in grading smoked chub. An 8-point scale was used to score the chub for general appearance, gloss, smoothness, firmness, oiliness, conformation defects, natural fish color, both internal and external smoked color, and aroma (see Table 1 footnote). Descriptors of quality were established from previous consultations with personnel from three New York City smoked fish processing plants, New York City delicatessen and supermarket smoked fish buyers, and a scientific advisor to the smoked fish industry. A backward elimination analysis of variance procedure (Helwig and Council 1979) was used to show association of independent variables with the dependent variable general appearance.

Table 1. Means, standard deviations and ranges of values for physical measurements and quality characteristics of commercially processed chub.[1]

Measurement	Mean	Std. Dev.	Minimum Value	Maximum Value
Length cm	25.41	.99	23.0	28.0
STD length (w/o tail) cm	21.15	.93	20.0	24.0
Head length mm	44.85	3.16	40.0	51.0
Weight g	122.18	13.68	103.0	169.0
Depth mm	50.54	3.71	44.0	63.0
Width mm	25.18	1.65	22.0	30.0
Body wall thickness mm[2]	7.44	1.10	5.0	9.5
Quality Characteristic[3]				
General appearance	5.38	1.04	3.0	7.0
External smoke	5.28	.72	4.0	7.0
Gloss	6.38	.75	5.0	8.0
Smoothness	6.44	.68	5.0	7.0
Firmness	6.13	.66	5.0	7.0
Defects	6.00	1.08	4.0	7.0
Natural Color	7.08	.58	6.0	8.0
Oiliness	3.67	.66	3.0	5.0
Aroma	6.62	.54	6.0	3.0
Muscle separation	6.62	1.66	2.0	8.0
Internal smoke	7.03	.74	5.0	8.0

[1]N = 39.
[2]Ventral body wall thickness measured anterior to anal fin 5mm off midline.
[3]Values based on an 8-point scale (1 = very unacceptable, 8 = very acceptable for all attributes except oilness where 1 = extremely oily and 8 = extremely dry).

Thirteen of the regular smoked chub were sampled to determined variation in percent moisture, NaCl and SWP. They were divided into right and left sides and then into dorsal and ventral portions. The dorsal muscles were further subdivided into approximately equal length anterior (A), center (B), and posterior (C) sections. Analyses were done on samples from each area of the fish. Additional commercially smoked chub processed in both convection type ovens and controlled environment smokehouses were purchased according to market quality and analyzed for salt and moisture. The dorsal muscles of two hundred four chub of each quality group (highly acceptable, acceptable, and unacceptable) processed in a convection oven were sampled. Similarly, chub processed in a controlled environment smokehouse and divided into acceptable (N = 238) and unacceptable (N = 108) categories by the processor were sampled and analyzed. Residual salt levels were determined by the modified A.O.A.C. procedure (1980). Moisture was determined by drying to a constant weight in a convection oven (A.O.A.C. 1980). Salt content in the water phase (SWP) was calculated from the salt and moisture values by the method described in the code of Federal Regulations, Title 21, Chapter 1, Part 122.3d (FDA 1980). Variations among anterior, center, and posterior sections of dorsal muscles were determined. Sources of variation and differences among least squares means were determined according to the procedure described by Helwig and Council 1979.

Development of Uniform Brining Procedure

A series of studies was conducted to determine the effect of brining, leaching, hanging (salt equalization) and smoking on moisture, salt, and SWP content of chub. For all studies, frozen chub were periodically received from New York fish processors and kept frozen (−14.4 °C) until needed. Thawing occurred in running tap water (20.6–24.4 °C). Brine to fish ratio was 2 to 1 by weight. Moisture, salt, and SWP were determined as previously described.

Initially, salt penetration into the dorsal musculature of chub and the effects of brine concentration and time in brine on residual salt content after hanging were determined. The thickest part of the dorsal muscle was dissected into external (E), middle (M), and internal (I) layers by separating the dorsal muscle longitudinally into approximately equally thick sections (Fig. 1). Brining took place at 2.2–3.3 °C (36–38 °F) in 6.6% (25° salometer) or 9.2% NaCl (35° salometer) brine for 16, 20, or 24 h. Sampling occurred after the brined chub hung in a 3.3 °C (38 °F) cooler for 14 h.

After locations of highest and lowest salt concentrations had been determined, interrelationships of brining, leaching, hanging and smoking were studied. In Study I, 22.7 Kg of chub were separated by weight and brined at 3.3 °C (38 °F) in either 6.6% or 7.9% NaCl solutions for 16 or 24 h. Four chub from each brine-time treatment group were selected immediately after brining for chemical analyses and eight chub from each group were leached by one of three methods:

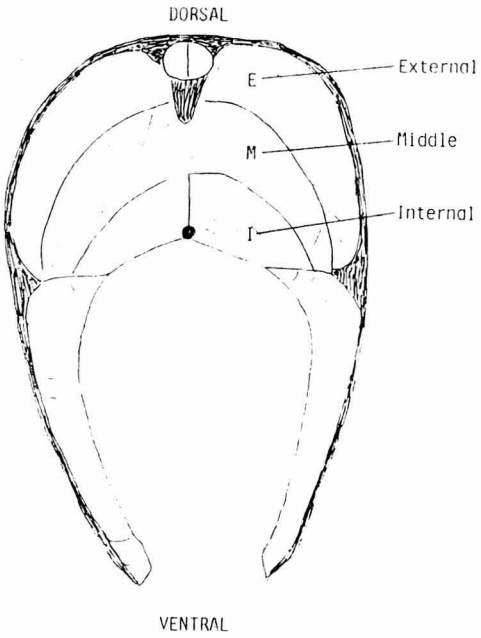

FIG. 1.
CROSS-SECTIONAL VIEW OF CHUB DORSAL MUSCLE INDICATING SAMPLING AREAS, E, M, AND I

20QT, 20QC, or 20RT. Chub leached by method 20QT were placed in a 18.9 L container which was filled with tap water, stirred initially, and allowed to stand at room temperature (approximately 25 °C) for 20 min. Method 20QC was identical to method 20QT except cold (3.3 °C) water was used for leaching. For method 20RT, the filled leaching vessel was flushed with tap water for 20 min at a rate to permit a slight overflow. Four chub from each brine-time-leach group were sampled for chemical analyses after leaching and the remaining four were sampled after hanging overnight at 3.3 °C (38 °F).

An additional lot of chub (Study II) was separated into three weight groups Small (Sm) = < 101g; Medium (Med) = 102–105g; Large (Lg) = 126–150g) and brined in 6.6% NaCl (25 ° salometer) for 16 h (Group 25/16) or 24 h (Group 25/24). Chub from each brine weight group were leached with chilled water (3.3 °C) by one of the following methods: Quiescent water for 20 min (20QC) or 40 min (40QC); running water for 20 min (20RC) or 40 min (40RC). All brined chub were hung for 14 h at 3.3 °C. Dorsal muscles for four Sm and Med and one Lg chub were sampled after equalization for chemical analyses. The remaining

chub were processed in a controlled environment smokehouse (Alkar Model JT 3497) for 1 h at each 32.2 °C (90 °F), 43 °C (110 °F), and 53.1 °C (130 °F) dry bulb (db) and then smoked for 1.5 h at 61.3 °C (150 °F) db and 53.9 °C (132 °F) wet bulb (wb).

In Study III, 528 chub were sorted into weight groups (SM = 63–96g; Med 1 = 97–111g; Med 2 = 112–134g; and Lg = 135–395g), brined in 6.6% NaCl for 16 h and leached in chilled water for 20 min(Method 20QC)or in 2.0% NaCl for 24 h (Method 2N/24). Smoke processing was accomplished by the procedure described previously. Chub were sampled for moisture and NaCl analyses after leaching and smoking. Percent SWP was calculated.

Approximately 320 additional chub (Study IV) were sorted into weight groups (Lg 1 = 125–149g; Lg 2 = 150–174g; Lg 3 = 175–200 g) and assigned to brine-leach treatment groups 25/16 - 20QT (6.6% NaCl for 16 h/20 min tap water leach); 25/16 - 2N/24 (6.6% NaCl for 16 h/2.0% NaCl for 24 h); 25/16 - 2N/14 (6.6% NaCl for 16 h/2.0% NaCl for 14 h); 30/16 - 2N/24 (7.9% NaCl for 16 h/2.0% NaCl for 24 h) or 30/16 - 2N/14 (7.9% NaCl for 16 h/2.0% for 14 h). Chub from each brine-leach-weight group were sampled for chemical analyses before and after thermal processing. The industry-type smokehouse schedule described previously was used. Treatment means from all studies were subjected to analysis of variance and Fisher Least Significant Difference (LSD) tests (Helwig and Council 1979).

RESULTS AND DISCUSSION

Characterization of Commercially Produced Smoked Chub

Generally, the commercially smoked chub most preferred by fish processors and retailers weighed more than 144 g (5 oz.), were a uniform golden brown color, smooth and firm but not hard in texture (data not shown). They were thick in the dorsal portion indicating meatiness. But, 39 smoked chub randomly selected from a New York Processor's production line weighed from 103.0 - 169.0g, had a mean length of 25.4 cm, and varied in thickness of the ventral body wall. A backward elimination analysis of variance procedure showed that external smoked color, gloss, extent of product defects and internal smoked color were the most important attributes used by processors and retailers for determining general appearance of smoked chub (data not shown). Moisture, salt, and SWP values for 13 of these chub are presented in Table 2. As expected, analysis of variance showed very little variation between right and left sides. Greatest sources of variation were due to fish sampled, part (dorsal or ventral) and section (anterior, center, or posterior portion of the dorsal muscle). Least squares analysis indicated significantly lower percent moisture in the ventral muscle than

Table 2. Data summary and least squares analysis for 13 smoked chub processed by New York fish processsor

ANALYSIS OF VARIANCE

Source	Degrees of Freedom	% H_2O F-Value	% H_2O P . <F	% NaCl F-Value	% NaCl P . <F	% Salt in Water Phase F-Value	% Salt in Water Phase P . <F
Fish	12	3.42	0.002	86.39	0.001	102.42	0.001
Side	1	0.07	0.80	4.19	0.05	1.72	0.20
Part	1	8.07	0.007	55.67	0.001	85.64	0.001
Section (Dorsal)	2	5.12	0.01	24.42	0.001	39.99	0.001
Fish x Section	36	1.32	0.19	1.65	0.05	2.46	0.002
Error	52						
Standard Deviation		2.12		0.157		0.194	
R-Squared		0.696		0.963		0.971	
Means (Least Square)							
OVERALL		70.4		2.50		3.46	
SIDE							
Left		70.4		2.46		3.40	
Right		70.5		2.53		3.46	
PART[1]							
Dorsal		70.8^{a}		2.43^{a}		3.33^{a}	
Ventral		69.4^{b}		2.70^{b}		3.75^{b}	
SECTION[1]							
A - Anterior		70.9^{c}		2.53^{d}		3.47^{d}	
B - Center		71.7^{c}		2.24^{c}		3.02^{c}	
C - Posterior		69.7^{d}		2.51^{d}		3.48^{d}	
J[2]		69.4^{d}		2.70^{e}		3.75^{e}	

[1]Least squares means within main effects with different letters in the same column are significantly different ($P < .01$).

[2]J = Ventral portion duplicated to permit fish × section interaction analysis.

in the dorsal muscle of the chub. The ventral muscle was significantly higher in salt and SWP than the dorsal muscle. Lower values were noted for salt and SWP for the thicker center section (B) of the dorsal muscle compared to either the anterior (A) or posterior (C) end. The anterior and posterior ends of the dorsal muscle were not significantly different from one another.

Since both convection and controlled environment smokehouses are used in the industry, samples of chub processed in both types of houses were analyzed and the values compared. In Table 3, highly acceptable smoked chub processed in a convection oven contained significantly higher moisture and lower salt and SWP than the acceptable and unacceptable quality groups. Within the dorsal muscle, the thick center section (B) was significantly lower in percent SWP than either end (sections A and C). Similar results were noted for chub processed in a controlled environment smokehouse. Acceptable smoked chub were significantly lower in salt and SWP and higher in moisture than unacceptable smoked chub. Percent SWP was lowest in the center section (B) of the dorsal muscle. Mean values for percent moisture, salt and SWP were very similar for the highest quality chub from both smokehouses.

Table 3. Means for moisture, salt, and salt in the moisture phase by acceptability and section for chub smoked in convection and controlled environment type smokehouses

	Convection				Controlled Environment			
Acceptability[1,2]	N	% H_2O	% NaCl	% SWP	N	% H_2O	% NaCl	% SWP
0	204	72.7[a]	2.39[c]	3.18[c]	-	-	-	-
1	204	71.5[b]	2.91[b]	3.92[b]	238	72.8[a]	2.42[b]	3.19[b]
2	204	71.1[b]	3.45[a]	4.59[a]	108	69.1[b]	2.71[a]	3.72[a]
Section[2,3]								
A	-	71.8[a]	3.11[a]	4.17[a]	-	72.7[a]	2.62[a]	3.44[a]
B	-	72.4[a]	2.80[c]	3.73[c]	-	72.7[a]	2.37[b]	3.13[b]
C	-	71.0[b]	2.90[b]	3.87[b]	-	71.2[b]	2.44[b]	3.29[a]

[1]Acceptability – 0 = highly acceptable; 1 = acceptable; 2 = unacceptable.
[2]Means in the same column with different letters are significantly different ($P < .05$).
[3]Section A – Anterior portion of contralateral muscle; Section B – middle portion of contralateral muscle.

Development of Uniform Brining Procedure

As shown by the ranges in percent SWP (Fig. 2) after brining and hanging for 14 h, salt penetration varied greatly within layers (E,M,I) of the dorsal muscle for both brine concentrations and for all three times in brine. Generally, the external (E) and internal (I) layers of the dorsal muscle were similar in percent SWP within brines and times in brine. Percent SWP was higher for chub brined in 9.2% NaCl (35° salometer) than chub brined in 6.6% NaCl (25° salometer) brine. Also, percent SWP increased with increased time in brine for both brine concentrations.

Immediately after brining (Study I), chub brined in 7.9% NaCl brine were significantly higher ($P < .1$) in ventral SWP content than chub brined in 6.6% NaCl brine (Table 4). Also, the dorsal SWP content of chub brined in 7.9% NaCl brine for 24 h was significantly higher than that from other brining methods. The variation in percent SWP among dorsal and ventral portions receiving the same brine treatment was not appreciably reduced by either leaching method used in Study I (Table 4). Similar variation among chub sections remained after a 14 h equalization period in chub brined in 6.6% NaCl brine for 16 or 24 h.

In Study II (Table 5), percent SWP values were generally higher than those experienced in Study I (Table 4) for the same brine-leach treatment. After processing, chub were generally lower and more ideal (3.0–4.0%) in percent SWP when brined in 6.6% NaCl brine for 16 h rather than 24 h (Table 5). Similar

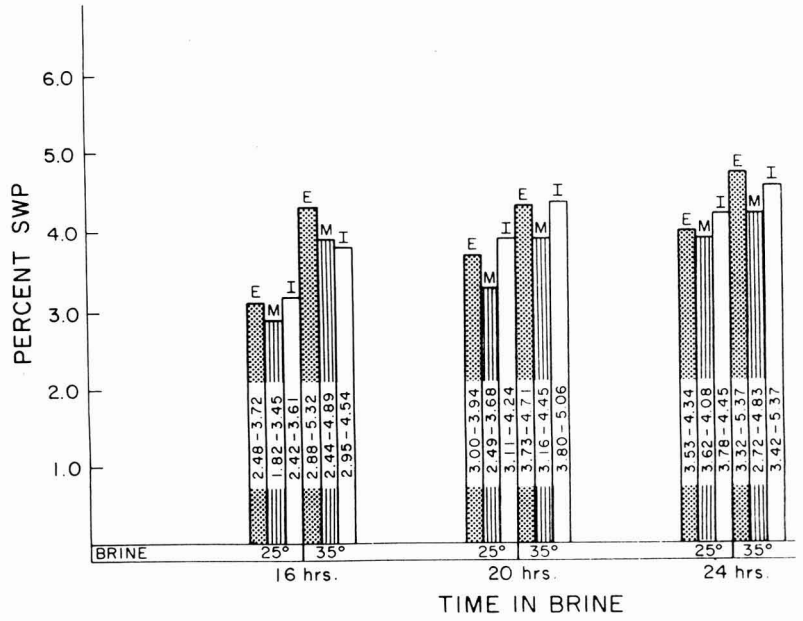

FIG. 2.
PERCENT WATER PHASE SALT OF EXTERNAL (E), MIDDLE (M), AND INTERNAL (I) AREAS OF THE DORSAL MUSCLE AFTER 16, 20 AND 24 h IN 6.6% AND 9.2% NaCl BRINES

weight chub receiving the same brine-leach treatment were not significantly different in % SWP between dorsal and ventral sections. But, leaching in running water instead of quiescent or for 40 min rather than 20 min did not improve % SWP after processing in all chub weight groups. Crean (1961) reported that fish surface area available for salt transfer is the biggest factor affecting the uniformity of salt uptake. Also, lowering the brine concentration during the second phase of a two-step brining process leached excess salt from the thinner (ventral) muscles and promoted NaCl penetration into the thicker dorsal muscles of mullet (Kosak and Toledo 1981).

Therefore, in Study III, the conventional leaching methods and equalization (hanging) time were replaced by a holding time in a low concentration salt solution. As shown in Table 6, chub sampled prior to thermal processing (after leaching) that had been brined in 6.6% NaCl for 16 h and then held in 2% NaCl for 24 h (Treatment 25/16–2N/24) were more uniform in % SWP among weight groups for both the dorsal and ventral sections than those leached by the conventional 20 min cold water (3.3 °C) leach (Treatment 25/16–20QC). In fact, %

Table 4. Effect of brine-leach method on percent water phase salt of chub sampled after brining, leaching and equalization.

Brining Method[1]	Section[2]	After Brining[3]	After Leaching[3,4,5]			After Equalization[4,6]		
			20 QT	20 QC	20 RT	20 QT	20 QC	20 RT
25/16	D	2.76^{a}	2.20^{a}	2.17^{a}	2.01^{a}	2.07^{a}	1.96^{a}	2.02^{a}
	V	4.53^{a}	3.20^{a}	3.14^{a}	3.00^{a}	3.10^{b}	3.52^{b}	3.11^{b}
25/24	D	2.94^{a}	2.55^{a}	2.68^{a}	2.60^{b}	2.40^{a}	2.84^{a}	2.73^{a}
	V	4.60^{a}	3.37^{a}	3.79^{b}	3.79^{b}	3.65^{b}	3.84^{b}	3.52^{b}
30/16	D	2.57^{a}	2.66^{a}	2.69^{a}	2.49^{ab}			
	V	5.58^{b}	4.33^{b}	4.19^{b}	3.98^{b}			
30/24	D	4.11^{b}	3.40^{b}	3.27^{b}	3.60^{c}			
	V	6.36^{c}	5.02^{c}	4.94^{c}	4.72^{c}			

[1]25/16 = chub brined in 6.6% NaCl for 16 hr.
25/24 = chub brined in 6.6% NaCl for 24 hr.
30/16 = chub brined in 7.9% NaCl for 16 hr.
30/24 = chub brined in 7.9% NaCl for 24 hr.
[2]D = Dorsal; V = Ventral.
[3]Means in the same column within fish sections with different lower case letters are significantly different ($P < .1$), N = 4.
[4]20 QT = 20 min leach in quiescent tap water; 20 QC = 20 min leach in quiescent 3.3 °C water; 20 RT = 20 min leach in running tap water.
[5]Means within some row are not significantly different ($P < .1$), N = 4.
[6]Means in the same column and row within brining methods with different letters are significantly different ($P < .1$), N = 4.

Table 5. Effect of brine-leach method on mean percent water phase salt of chub sampled after equalization and processing.

Brining Method[1]	Leaching Method[2]	After Equalization[3,4,5]						After Processing[3,4,5]					
		Sm		Med		Lg		Sm		Med		Lg	
		D	V	D	V	D	V	D	V	D	V	D	V
25/16[6]	20 QC	3.64^{ABCbc}	3.93^{Cc}	3.62^{ABde}	3.66^{ABCab}	3.78^{ABCc}	3.20^{Aabc}	3.60^{Aa}	3.98^{Aa}	3.79^{Aa}	4.08^{Aab}	3.83^{Aab}	3.96^{Aab}
	20 RC	3.45^{Aab}	3.37^{Aa}	3.59^{Acde}	3.68^{Abc}	3.60^{Ac}	3.88^{Ac}	4.07^{BCab}	4.29^{Cab}	3.63^{ABCa}	3.72^{ABCa}	3.21^{Aa}	3.60^{ABa}
	40 QC	3.32^{ABab}	3.36^{ABa}	3.14^{ABa}	3.44^{Bab}	2.84^{Aa}	2.88^{Aa}	4.21^{CDbc}	4.68^{Dbc}	3.95^{ABCab}	4.18^{BCDabc}	3.29^{Aa}	3.53^{ABa}
	40 RC	3.38^{Aab}	3.64^{Aabc}	3.32^{Aabc}	3.55^{Aab}	3.37^{Aabc}	3.30^{Aabc}	4.77^{Bd}	4.65^{Bbc}	3.99^{Aabc}	4.46^{ABbcd}	4.16^{ABbc}	4.25^{ABab}
25/24[7]	20 QC	3.65^{bc}	3.56^{ab}	3.36^{abcd}	3.31^{a}	3.06^{ab}	3.23^{abc}	4.68^{cd}	4.87^{c}	4.43^{bc}	4.53^{bcd}	4.22^{bc}	4.65^{b}
	20 RC	3.83^{c}	3.90^{bc}	3.77^{de}	4.02^{c}	3.50^{abc}	3.76^{c}	5.18^{d}	5.16^{c}	4.51^{c}	4.75^{d}	4.29^{bc}	4.63^{b}
	40 QC	3.27^{a}	3.54^{a}	3.20^{ab}	3.34^{ab}	3.25^{abc}	3.10^{ab}	4.86^{d}	4.92^{c}	4.48^{bc}	4.74^{d}	4.31^{bc}	4.59^{b}
	40 RC	3.64^{bc}	3.60^{abc}	3.50^{bcd}	3.54^{ab}	3.42^{abc}	3.66^{bc}	5.03^{d}	4.94^{c}	4.51^{c}	4.47^{bcd}	4.79^{c}	4.57^{b}

[1]25/16 = chub brined in 6.6% NaCl for 16 hr; 25/24 = chub brined in 6.6% NaCl for 24 hr.
[2]20QC = 20 min quiescent leach in 3.3 °C water; 20 RC min 3.3 °C running water leach; 40 QC = 40 min quiescent leach in 3.3 °C water; 40 RC = 40 min 3.3 °C running water leach.
[3]Sm = small chub; med = medium chub; lg = large chub.
[4]D = Dorsal muscle, V = Ventral muscle.
[5]Means in the same column with different lower case letters are significantly different ($P < .1$).
[6]For method 25/16, means in the same row within processing stage with different upper case letters are significantly different ($P < .1$)
[7]For method 25/24, means in the same row within processing stage are not significantly different ($P < .1$).

Table 6. Effect of leaching method on percent water phase salt in chub after leaching and after processing in Study III[1] [2]

Weight Group	Section[3]	After Brining[4,5]	After Leaching[5,6]		After Processing[6,7]	
			20QC	2N/24	20QC	2N/24
63-96g (Sm)	D	3.30^{BC}	2.63^{Ca}	2.61^{Ba}	3.88^{Ea}	3.64^{DEa}
	V	3.39^{C}	2.63^{Ba}	2.59^{Aa}	4.41^{Eb}	3.85^{Ea}
97-111g (Med 1)	D	3.30^{BC}	2.21^{Ba}	2.64^{Bb}	3.12^{CDa}	3.13^{BCDa}
	V	3.37^{C}	2.25^{ABa}	2.58^{Aa}	3.89^{Ea}	3.62^{CDEa}
112-134g (Med 2)	D	3.01^{AB}	1.96^{ABa}	2.58^{ABb}	2.74^{BCa}	3.08^{BCa}
	V	3.25^{BC}	2.15^{Aa}	2.60^{Ab}	3.32^{Da}	3.49^{BCDEa}
135-301g (Lg)	D	2.77^{A}	1.71^{Aa}	2.18^{Ab}	1.96^{Aa}	2.50^{Aa}
	V	3.12^{BC}	1.89^{Aa}	2.42^{Aa}	2.39^{ABa}	3.05^{ABa}

[1]N = 11.
[2]Means in the same row within section and processing stage followed by different low case letters are significantly different at $P < .01$ (Fisher's LSD).
[3]D = dorsal muscle; V = ventral muscle.
[4]25/16 = chub brined in 6.6% NaCl for 16 hr.
[5]Means in the same column within section followed by different upper case letters are significantly different at $P < .01$ (Fisher's LSD).
[6]20 QC = 20 min quiescent leach in 3.3 °C water; 2N/24 leached in 2% NaCl for 24 hr.
[7]Means in the same column followed by different uppercase letters are significantly different at $P < .01$ (Fisher's LSD).

SWP values of chub leached in 2% NaCl were very similar for the dorsal and ventral sections of chub weighing <135 g (wt. grps. Sm, Med 1, Med 2). After processing by the industry schedule, dorsal sections of chub leached in the 2% NaCl solution (Treatment 25/16–2N/24) were more uniform in percent SWP (2.50–3.64) for all weight groups than dorsal sections of Treatment 25/16–20QC chub leached in 3.3 °C (38 °F) water for 20 min (1.96–3.88). A similar uniformity in percent SWP among ventral sections of processed chub was noted with Treatment 25/16–2N/24 ranging from 3.05–3.85% SWP as compared to 2.39–4.41% SWP for the 20 min cold water leach (Treatment 25/16–20QC). Chub brined by the 2% NaCl leaching procedure (Treatment 25/16–2n/24) contained the more desirable percent SWP for both the light and heavy weight groups. In contrast, light weight chub brined and leached conventionally in cold water for 20 min (Treatment 25/16–20QC) were too high in percent SWP while heavy chub brined by this procedure contained too little water phase salt in both thick and thin sections.

The effect of holding time in the 2% salt solution was investigated and compared to the 20 min cold water leach (Study IV). Only processed chub brined by method 25/16–20QC (6.6% 16 h/20 min leach) exhibited significant ($P < .01$) percent SWP variation among weight groups (Table 7). Variation between dorsal and ventral sections was significant ($P < .01$) for all weight groups brined by method 25/16–20QC and in Sm and Med chub brined by method 25/16–2N/24

and 30/16–2N/24. Combined weight group data (Table 8) showed methods 25/16–2N/24, 25/16–2N/14, 30/16–2N/24 and 30/16–2N/14 to have much lower standard deviations than method 25/16–20QC. Method 30/16–2N/14 produced chub somewhat higher in % SWP than methods 25/16–2N/24, 25/16–2N/14 and 30/16–2N/24. Method 25/16–2N/24 produced chub with less variation in percent SWP for both dorsal and ventral sections than method 25/16–2N/14.

SUMMARY AND CONCLUSIONS

Although fish processors and retailers expressed a preference for uniform golden brown smoked chub weighing >144 g, processed chub from the production line of a New York processor ranged in weight for 103.0 – 169.0 g and differed greatly in thickness of the ventral body wall. A backward elimination analysis of variance showed that smoked chub produced for the New York area market were usually evaluated at point of purchase according to their external and internal smoked color, gloss, and the extent of physical deformities (splays, splits, etc.). They varied significantlly in SWP among chub and between dorsal and ventral sections of the same fish. Industry assessment of quality for the finished commercial product produced in both convection and controlled environment smokehouses was related to moisture and salt content with the acceptable quality chub containing about 3.2% salt in the water phase.

Brining studies revealed that salt penetration into the muscle was influenced by brine concentration, time in brine, and size of fish. Generally, the external and internal (near body cavity) layers of the dorsal muscle (thickest section of the fish) were similar after brining and hanging for 14 h in percent SWP within brines and times in brine. Conventional leaching procedures did not equalize SWP in chub after processing. Therefore, a two-stage brining procedure (6.6% NaCl/16 h followed by 2% NaCl/24 h) was used to reduce the variation of SWP among dorsal and ventral portions of chub (weighing 63–134g) after the smoking process was completed. Ranges in SWP among chub in these studies indicate that modifications in brine concentration and/or time in brine may be necessary for larger chub.

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Table 7. Percent water phase salt in chub after processing in Study IV [1] [2] [3]

Brine-Leach[5] Method	Section[6]	Weight Groups[4] Sm[7]	Med[7]	Lg[7]
25/16 - 20 QC	D	3.61^{BCb}_{Db}	3.36^{BCb}_{Eb}	2.70^{Aa}_{BCDa}
	V	3.99	3.97	3.31
25/16 - 2N/24	D	3.25^{Aa}_{CDa}	2.95^{Aa}_{BCa}	3.05^{ABCa}_{DEa}
	V	3.70	3.43	3.64
25/16 - 2N/14	D	3.36^{ABa}_{BCDa}	3.12^{ABa}_{BCa}	2.94^{ABa}_{BCDa}
	V	3.68	3.38	3.40
30/16 - 2N/24	D	3.37^{ABa}_{CDa}	3.20^{ABa}_{CDEa}	2.89^{ABa}_{BCDa}
	V	3.78	3.61	3.34
30/16 - 2N/14	D	3.68^{BCDa}_{Da}	3.47^{BCDa}_{DEa}	3.48^{CDa}_{Fa}
	V	4.01	3.83	4.01

[1]Values are mean of eight observations for small and medium weight groups and four observations for the large weight group.
[2]Means in the same column followed by different upper case letters are significantly different at P $<$.01 (Fisher's LSD).
[3]Means in the same row followed by different lower case letters are significantly different at P$<$.01 (Fisher's LSD).
[4]Values are percent water phase salt.
[5]25/16 - 20 QC = chub brined in 6.6% NaCl for 16 hr; leached 20 min in quiescent 3.3 °C water.
25/16 - 2N/24 = chub brined in 6.6% NaCl for 16 hr; leached in 2% NaCl for 24 hr.
25/16 - 2N/14 = chub brined in 6.6% NaCl for 16 hr; leached in 2% NaCl for 14 hr.
30/16 - 2N/24 = chub brined in 7.9% NaCl for 16 hr; leached in 2% NaCl for 24 hr.
30/16 - 2N/14 = chub brined in 7.9% NaCl for 16 hr; leached in 2% NaCl for 14 hr.
[6]D = dorsal muscle; V = ventral muscle.
[7]Sm = 125 - 149 g. chub, Med = 150 - 174 g chub, Lg = 175 - 200 g chub.

Table 8. Percent water phase salt, ranges, and standard deviations of chub after processing in Study IV.

Brine-Leach[1] Method	Section[1]	All Weight Groups Combined Sm, Med, Lg Percent[2] SWP	Standard Deviation	Range	Min. Value	Max. Value
25/16 - 20 QC	D	3.33	0.43	1.45	2.50	3.95
	V	3.85	0.43	1.37	2.99	4.36
25/16 - 2N/24	D	3.09	0.36	1.25	2.45	3.70
	V	3.58	0.32	1.21	3.06	4.27
25/16 - 2N/14	D	3.18	0.36	1.48	2.45	3.93
	V	3.50	0.39	1.64	2.54	4.18
30/16 - 2N/24	D	3.21	0.35	1.22	2.62	3.84
	V	3.62	0.35	1.28	3.02	4.30
30/16 - 2N/14	D	3.56	0.31	1.21	2.97	4.18
	V	3.94	0.30	1.11	3.31	4.42

[1]Explanations of brine-leach method and sections are given in Table 7.
[2]Values are mean of 20 observations.

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KINETICS OF THERMAL SOFTENING OF FOODS — A REVIEW

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ABSTRACT

Methods for measuring thermal softening of foods are reviewed. The principal physical tests for softening are based on puncture, shear, back extrustion, and deformation. Sensory scores for softening are based on 9-point scales. Few studies on kinetics of thermal softening of foods have taken thermal lag and uneven heating of sample into consideration. Published data on thermal softening of foods are tabulated in terms of apparent first order rate constants and activation energies.

INTRODUCTION

Foods of economic importance can be classified as cereals, legumes, fruits, vegetables, meat, sea foods, and products derived from them. Most foods are either stored or processed so that they can be consumed long after they have been harvested. Storage temperatures for foods are relatively low (approximately −10 °C to 20 °C) and they are kept for long times (up to a year). In contrast, during processing, foods are subjected to temperatures of about 84 ° to 121 °C in operations such as blanching and sterilization. The residence times during these operations range from a few minutes for blanching to about an hour for conduction heated foods in large cans. The textural characteristics of the foods change as a result of many chemical changes during storage and processing. In general,

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many foods soften during storage and processing. Knowledge regarding the softening phenomena will be useful in improving the design of storage facilities and processing schedules. In particular, kinetics of softening can lead to improved design of thermal processes for foods.

Microbial and chemical changes (such as the loss of vitamins and degradation of chlorophyll) in foods during thermal processing have been studied extensively (Thompson and Norwig 1983). Softening of foods in general and the kinetics of softening in particular have not received much attention. For example, softening of foods has not been discussed in review studies such as that of Hoyem and Kvale (1977). Most of the available information on kinetic parameters of softening of foods has been summarized in review articles by Lund (1975; 1982; 1983). Techniques for measuring softening of foods as well as the precautions to be taken in conducting the kinetics studies have not been reviewed. These are discussed in this paper, along with a summary of literature values of kinetic parameters and the structural changes due to heating, particularly during thermal processing.

KINETIC MODELS

A number of chemical changes take place when foods are subjected to a thermal process. For example, in meats the muscle fibers and connective tissues are affected by heat resulting in either softening or firming of the tissue. Because of the complex chemical composition of foods, it has not been possible to quantify all the changes taking place as a result of heating and to relate, in a quantitative manner, the chemical changes to physical changes such as softening. A simple and useful approach in softening studies has been to express data in terms of either apparent reaction rate constants (Eq. 1) or, analogous to microbial death kinetics, in terms of the D-value.

$$\frac{dP}{dt} = -k_n P^n \qquad (1)$$

where P is the property used to characertize softening, t is time, k_n is the reaction rate constant, and n is the order of change. The negative sign in Eq. 1 indicates that the magnitude of the property at a constant temperature decreases with time. For materials that soften upon heating, this is true for a quantity such as puncture force but for a parameter such as deformation there will be an increase with time and Equation (1) should be written without the negative sign. If the time dependence of the parameter P is first order ($n=1$), then it can be expressed as the D-value. The D-value is the time in minutes for a one log cycle

change of a property at a constant temperature. The D-value and the first order reaction rate constant are related by the equation:

$$k_1 = \frac{2.303}{D} \qquad (2)$$

In addition to describing the change in a property as a function of time at a fixed temperature, one must be able to describe the effect of temperature on the property. The Arrhenius relationship can be used to describe the effect of temperature on the reaction rate constant:

$$k = K_T \exp(-E_a/RT) \qquad (3)$$

Where E_a is the activation energy (calories/mole), R is the gas constant, T is the absolute temperature (°K), and k_T is a constant.

The z-value is used in microbiology to characterize the influence of temperature on the D-value and it is the temperature change which results in a ten fold change (one log cycle) in the D-value. The z-value and E_a are related (Lund 1975) by:

$$E_a = \frac{2.303\, R\, T\, T_{ref}}{z} \qquad (4)$$

The Q_{10} value is used as a measure of the temperature coefficient of chemical and biological reactions and is defined as the change in the reaction rate constant for a change of 10 °C:

$$Q_{10} = \frac{k(T + 10\,°C)}{k(T)} \qquad (5)$$

For many chemical reactions the Q_{10} value is about 2.5–4. The relationship between Q_{10} and z value is:

$$z = \frac{18}{\log Q_{10}} \qquad (6)$$

EXPERIMENTAL METHODS FOR STUDYING SOFTENING

In order to obtain data on softening suitable for determining kinetic parameters, a food sample must be subjected to different temperatures for different time periods. It would be preferable to employ at least five different temperatures and, at each temperature, at least five different time periods. In general, softening rates of foods are higher than thermal degradation of vitamins; therefore, the time periods for experiments on softening must be relatively short in order to avoid excessive softening. It is important to note that the food must be subjected to conditions similar to those under which the kinetic data will be applied. For example, the heat and mass transport phenomena during the heating of canned black beans are different than when the beans are cooked directly in boiling water. The use of different sizes of a given food also can result in different magnitudes of the kinetic parameters.

Correction for Thermal Lags

A major deficiency with many studies on softening has been the absence of corrections for thermal lag, which is the determination of the equivalent minutes of heating at the test temperature due to uneven heating of the food samples. Furthermore, very often significant softening occurs by the time the food sample reaches the test temperature. In general, the measured property (e.g., extrusion force) will be an average value for the entire sample and the nonuniform softening during a test must be considered mathematically. Ideally, the tests and computations should be performed in such a manner so that the magnitudes of kinetic parameters for softening will be independent of the sample size.

Hayakawa *et al.* (1977) presented an iterative procedure for thermal lag correction in which the history of the center temperature of a cylindrical container (can) can be used to estimate the transient temperature distribution of eleven iso-j regions. This lag correction method has been employed for softening studies by other workers (Rao *et al.* 1981; Silva *et al.* 1981a,b). This method is relatively simple to use and the results are comparable to using elaborate schemes such as the numerical integration of the transient heat conduction equation (Teixeira *et al.* 1969).

To illustrate the effect of thermal lag on the process time at a given temperature, the process and equivalent isothermal times of Hayakawa and Timbers (1977) on peas in 211 × 011 cans are presented in Table 1. The significant differences between the two quantities for a food generally assumed to be heated by convection in a small can must be noted. It must be emphasized that the thermal lag effect will depend not only on the size of the container but also on the food under investigation. For these reasons, correction for thermal lag must be determined for each test.

Table 1. Processing times and the equivalent isothermal times corrected for lags for peas in 211 × 011 cans[a]

Temp (°F)	Processing time code I	II	III	IV	V
	(Retort Time — min)				
175	10	30	50	80	120
200	5	15	25	45	60
225	5	10	20	30	45
250	1	3	6	10	20
275	0.75	1.5	3	6	15
300	0.5	1	2	4	8
	Equivalent times — min				
175	9.3	29.5	49.4	79.5	118.5
200	4.7	14.2	24.4	44.4	59.2
225	4.5	9.2	19.6	29.4	44.3
250	0.35	2.5	5.3	9.3	19.5
275	0.2	1.0	2.1	5.1	14.3
300	0.12	0.5	1.3	3.25	7.45

[a]Source: Hayakawa *et al.* (1977)

Correction for Uneven Heating of Sample

When large food samples are employed, such as in cans or large pieces of food, the softening will not be even throughout the sample. Further, in general, the experimentally measured value of softening is an average for the entire sample. For example, the back extrusion force for a can of vegetables is the average value for all the vegetable pieces that were softened to different levels as a result of their different locations in the can. The concept of iso-j regions can be used also for determining the average value of softening or any other quality parameter (Stumbo 1973; Hayakawa *et al.* 1977) in a can. Indeed, the correction for thermal lag and the correction for uneven heating of a sample can be combined in a single computer program (Rao *et al.* 1981).

Objective Methods for Measuring Softening

There are many objective methods for measuring the softening of foods. The methods are the outcome of a great deal of interest in the textural properties of

Table 2. Techniques for objective measurement of softening

Fruits and Vegetables	Legumes
Puncture force	Puncture force
Deformation	Back extrusion force
Back extrusion force	
Beef and Poultry Meats	Sea Foods
Warner-Bratzler	Shear and cutting force
Rice	Spaghetti
Compressibility, viscosity, cohesiveness, pressed area	Cutting force

foods. Historically, methods for the objective measurement of texture have been developed for each commodity. For example, the Magness-Taylor punch test has been used to determine the maturity of apples and the Warner-Bratzler apparatus has been employed with meats. Nevertheless, one can encounter apparatus developed for a specific food being employed for other foods so that there do not exist hard and fast rules for the use of every texture measuring instrument. Many of the tests have been modified with improved instrumentation. Most of the objective methods are based on the precise measurement of either a force or a distance with a Universal Testing Machine. The objective methods for various foods are summarized in Table 2 and they are briefly described here.

Fruits and Vegetables. Numerous sudies have been conducted on the objective measurement of the texture of fruits and vegetables. Tests commonly employed for fruits and vegetables are: measurement of deformation, puncture force, and back extrusion force (Bourne 1980; 1982a).

Legumes. For legumes the puncture force and the back extrusion force have been employed as indicators of softening (Bourne 1972; Rao *et al.* 1981; Silva *et al.* 181a,b).

Meats. The Warner-Bratzler apparatus has been employed for the objective texture measurement of meats (Harris 1976).

Rice. Thermal softening of rice accompanied by water absorption has been studied more than other cereal grains. Compressibility, viscosity, cohesiveness, and area upon pressing the cooked grains between plates (Pillaiyar and Mohandoss 1981) have been used as objective measures of softening of rice.

Seafoods. The forces necessary to shear and cut have been employed as indicators of softening (Deng 1981; Ma *et al.* 1983).

Spaghetti. For spaghetti, the force for cutting has been used as the measure of softening (Matsuo and Irvine 1971).

Although an extensive literature survey was not conducted, it appears that few other foods have been the subjects of softening studies.

Sensory Evaluation of Softening

Softening can be evaluated by sensory panels. In studies on green beans, corn, peas, and asparagus (Hayakawa *et al.* 1977), black beans (Silva, *et al.* 1981a), and shrimp (Ma *et al.* 1983) a 9 point scale was employed (1 = extremely soft and 9 = extremely tough). Generally, the subjective and objective measures of softening are linearly related, and a large change in the objective measure is reflected as a small change in the sensory panel score. This can be seen in Fig. 1 for black beans where a change in the puncture force from 75g to 600g resulted in a change in the sensory score from 3 to 8. Indeed, the relationship between the

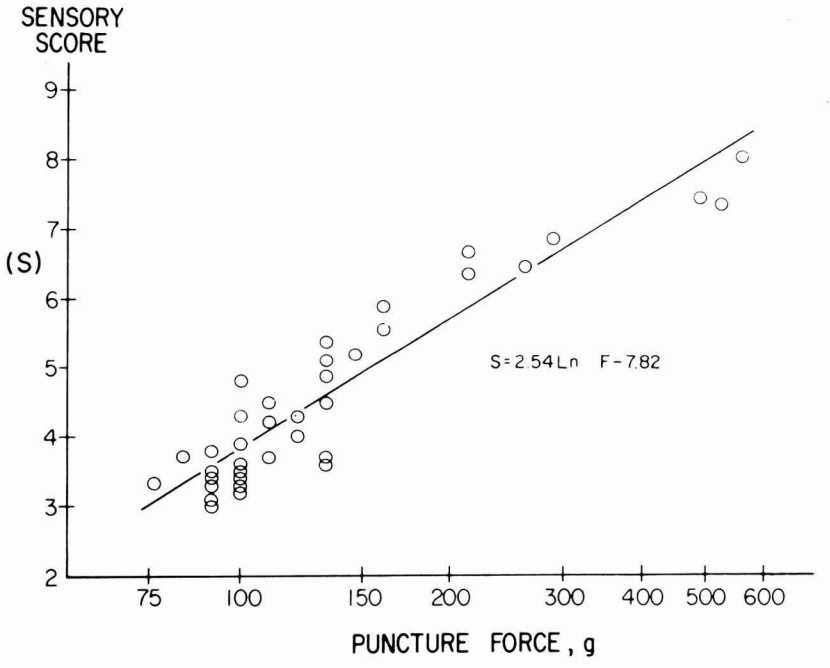

FIG. 1.
PUNCTURE FORCE AND SENSORY SCORES OF BLACK BEANS (source: Silva *et al.* 1981a)

puncture force and the sensory score could be described by the equation:

$$\text{Sensory Score} = 2.54 \ln (\text{Puncture Force, g}) - 7.82 \quad (6)$$

Harada *et al.* (1985a) employed a 11 point scale (1 = completely raw/very hard, 6 = optimal texture, 11 = completely overcooked/pulpy) for potatoes and the correlation between sensory score and shear force (N) was:

$$\text{Sensory Score} = 7.65 - 3.85 \log (\text{Shear Force, N}) \quad (7)$$

There can be exceptions to this general observations as shown in Fig. 2, where a change in the shear force from 1N to 5N resulted in a change in the sensory score from about 1 to about 6.5. The linear correlation between shear force and sensory score was described by the equation:

$$\text{Sensory Score} = 1.38 (\text{Shear Force, N}) + 0.26 \quad (8)$$

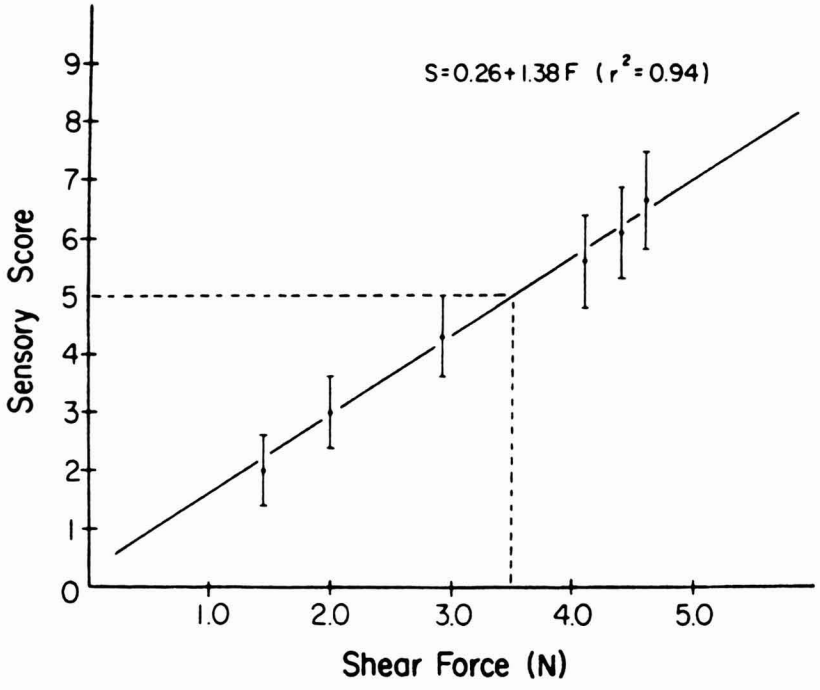

FIG. 2.
SHEAR FORCE AND SENSORY SCORES FOR SHRIMP (source: Ma *et al.* 1983)

Steven's Law Parameters for Black Beans and Shrimp

The puncture force, sensory scores data of Silva *et al.* (1981a) on black beans and the shear force, sensory scores data of Ma *et al.* (1983) on shrimp can be used to test the applicability of Steven's law and to determine the parameters of the model:

$$S = C F^n \qquad (9)$$

where, S is the sensory score, F is the objective measure of texture (puncture force or shear force), and C and n are constants to be determined.

From the tabulated data on puncture force and sensory scores for black beans in Silva *et al.* (1981a) we calculated C and n to be 0.542 and 0.427, respectively. In the case of shrimp, tabulated data of shear force, sensory scores were not readily available. Therefore, sensory scores were calculated using Eq. (7) for selected values of shear force. The coefficients C and n for the calculated shear force, sensory scores were 1.61 and 0.919, respectively.

The magnitudes of the exponent being <1 for both black beans and shrimp confirms that perceptual system contracts the objective measure of texture (Moskowitz and Kapsalis 1976). However, the different magnitudes of n indicate that it depends on the objective measure being used to correlate with the sensory scores. Further, the dependence of the magnitude of n on the commodity under study can not be ruled out.

EFFECT OF CHEMICAL AND PHYSICAL CHANGES ON TEXTURE OF FOODS

Texture of foods is affected by chemical and physical changes which have occurred as a result of storage, processing, and thermal processing. Chemical and structural changes of fruits, vegetables, and meats and the concomitant textural changes have received considerable attention.

Chemical Changes in Fruits and Vegetables

Chemical changes as a result of heating lead to a change in texture. Van Buren (1979) discussed softening in the case of fruits and vegetables and pointed out that the chemical changes that take place in the cell wall and middle lamella components are important. In the case of edible plants, primary cell walls are of chief interest. Secondary cell walls are nearly absent in mature fruits and their presence in appreciable amounts in vegetables makes them too tough and fibrous.

The cell wall is made up of cellulose fibrils imbedded in a matrix consisting largely of pectic substances, hemicelluloses, proteins, lignins, lower molecular weight solutes, and water. The percentages of pectic substances, hemicelluloses, and cellulose in the primary wall are about equal. As a simple explanation, it can be said that cellulose gives rigidity and resistance of tearing, while the pectic substances and hemicellulose confer plasticity and the ability to stretch. The middle lamella may be considered to be an extension of the matrix cell wall material but without the cellulose materials.

Fruits and vegetables soften when heated in part due to the loss of turgor (particularly leafy vegetables), but also due to complex chemical changes in the cell wall matrix polysaccharides. The changes are influenced by factors such as pH and the types and quantities of salts that are present. The uptake of water by polysaccharides can reduce the cohesiveness of the cell wall matrix and decrease the intercellular adhesion. A high degree of methoxylation of cell wall pectin can increase water uptake. Demethoxylation of pectic substances catalyzed by the enzyme pectin methyl esterase is important for the texture of fruits and vegetables. The enzymes is activated when a plant tissue is bruised or frozen, or heated to 50–80 °C. Demethoxylation usually results in a firmer texture of fruits prior to thermal processing and of vegetables after thermal processing. Undesirable degrees of softness during heat processing may be reduced by the addition of calcium salts prior to processing. In order to avoid off flavors, the addition is rarely more than 1% of the weight of the fruit or vegetable.

Structure and Toughness of Meat

The structure of striated muscle can be considered as basically a two component system made up of muscle fibers and intramuscular connective tissue (Harris 1976). Changes in myofibrillar structure in the period between slaughter and the full development of rigor mortis can greatly affect tenderness of the meat. Changes in the myofibrillar structure also produce concomitant changes in the connective tissue network. As the muscle fiber contracts along its length there is an increase in the angle between the collagen fibers of the network and the main axis of the muscle fiber. Both the sarcomere length in the muscle fibers and the orientation of the collagen fibers in the connective tissue network are affected.

Causes for Toughness of Meat. Myofibrillar contraction to sarcomere lengths less than 1.8–2.0 μm increases toughness in the cooked postrigor meat. However, at sarcomere lengths 1.2–1.3μm and below, the meat becomes tender eventually becoming as tender as that at sarcomere lengths greater than 1.8–2.0 μm (Harris 1976). The increased tenderness of very severely cold-shortened muscle (sarcomere lengths 1.2–1.3μm) is attributed to the severe structural disruption that produces zones of stretched as well as contracted myofibrils. Because adhesion between meat fibers increases significantly with myofibrillar contraction, connective tissue also plays a part in cold-shortened toughness.

Phases of toughness. There are two separate phases of toughening with increasing cooking temperature (Bouton *et al.* 1981): (1) in the first phase, 3–4 fold toughening between 40–50 °C, and (2) further doubling between 65 and 75 °C. This phenomena can be explained in terms of the relative contributions of the myofibrillar and connective tissue structures. While the myofibrillar structural changes were reflected in increased initial yield force values with a Warner-Bratzler apparatus, the connective tissue contributions decreased as the temperature was raised about 50 °C. The connective tissue contributions depended on the age of the animals as well as the cooking temperature. Softening due to prolonged cooking is probably due to conversion of collagen to gelatin and dissociation of muscle proteins.

DATA ON THERMAL SOFTENING OF FOODS

There is a large body of information on softening of foods, and in some cases kinetic parameters such as a rate constant and the energy of activation can be calculated. However, as previously indicated, in many studies corrections for thermal lag and integration of the softening effect over the entire test piece of the food (or the container of the food) have not been undertaken. In this section, we present data on thermal softening of foods and discuss review articles on the subject.

Thermal Softening of Vegetables

Hayakawa *et al.* (1977) evaluated subjectively the softening of whole kernel corn, peas, and cut green beans. The heat processed samples were evaluated with respect to frozen control samples on a 1 to 9 scale, with 1 indicating no difference from control. A score of 4.0 was used to estimate kinetic parameters because the samples became objectionably poor at this score. Corrections were made for thermal lags during the thermal processing of the food samples in 211 × 011 cans. Rao *et al.* (1981) studied the loss of firmness, color, and vitamin C during thermal processing of peas in 303 × 406 cans. The thermal lag correction method of Hayakawa *et al.* (1977) was employed and the firmness of the peas was determined by the extrusion method (Bourne and Moyer 1968). The kinetic parameters were determined employing the ratio of the back extrusion force of the processed samples relative to the unprocessed sample. Loh and Breene (1981) determined kinetic parameters for potato discs (2.0 cm in diameter and 0.8 cm thick) and minimized the lag effects by eliminating data points in the initial heating stages.

Kinetic data also were reported on the thermal softening of carrots (Paulus and Saguy 1980) and cucumbers (Nagel and Vaughn 1954). However, corrections for thermal lags and averaging of the softening effect in the sample were not applied. The kinetic data on the softening of vegetables are summarized in Table 3.

Table 3. Kinetic parameters for softening of vegetables

Commodity	$k_{121}(min^{-1})$	E_a (kcal/mole)	Reference
Whole kernel corn	0.384	19.5	Hayakawa *et al.* (1977)
Peas	1.0	22.5	Hayakawa *et al.* (1977)
Cut green beans	0.576	22.0	Hayakawa *et al.* (1977)
Peas (extrusion)	0.250	18.5	Rao *et al.* (1981)
Carrots			Paulus and Saguy (1980)
Rothild (3mm)	0.494	27.2	
Kundulus (3 mm)	0.259	22.0	
Rubika (3 mm)	0.422	28.0	
Potatoes	0.516	28.0	Loh and Breene (1981)
Cucumbers	----	22.0	Nagel and Vaughn (1954)

Harada *et al.* (1985a) studied the kinetics of thermal softening of potato discs (3.0 cm in diameter and 0.6 cm thick) from three varieties in terms of perceived texture and taste as well as shear force. The study was conducted at 90°, 100°, and 110°C in a manner similar to that of an earlier study (Paulus and Saguy 1980). At a constant temperature, perceived texture and taste followed zero order equations and the rate constants at 110°C ranged between 1.32 and 1.52 min^{-1} for perceived texture and between 1.42 and 1.49 min^{-1} for taste. Changes in maximum shear force (N) at a constant temperature were described by first order equations and their magnitudes at 110°C ranged between 0.327 and 0.389 min^{-1}. The effect of temperature on the quality attributes was described by the z-value whose magnitude ranged between 17.2 and 20.4°C. The average shear force at optimal cooking (sensory score of 6) was 2.7 N. In a companion study, (Harada *et al.* 1985b) employed 21 potato varieties and studied the role of composition on thermal softening. A linear correlation was found between cell size of raw potatoes, C (μm) and optimal cooking time, t_{opt} (min):

$$t_{opt} = 28.93 - 0.14\ C,\ R^2 = 0.64 \qquad (10)$$

Dry matter content (%) at t_{opt} and shear force (N) at t_{opt} were also linearly correlated (R^2=0.45). However, no convincing correlations were found between pectin content and softening behavior.

Huang and Bourne (1983) suggested that thermal softening of vegetables is a two step process, both steps obeying apparent first order kinetics. For several

vegetables, the rate constants for the first step were at least 20 times greater than those of the second step. Bourne and Comstock (1985) suggested that greater firmness in low temperature blanched vegetables is due to chemical changes in the second step.

Thermal Softening of Legumes

Legumes are the main source of protein in many countires. Softening of dry beans has been attributed to changes in pectic substances (Sefa-Dedeh *et al.* 1978) and phytic acid phosphorous content (Moscoso *et al.* 1984).

Kinetic data on thermal softening were obtained by Silva *et al.* (1981a,b) for unsoaked black beans (*Phaseolus vulgaris* L.) and those soaked in distilled water and in a salt solution (2.5% sodium chloride, 1% sodium tripolyphosphate, 0.75% sodium bicarbonate, and 0.25% sodium carbonate). The puncture test (Bourne 1972) was used to measure the thermal softening and the lag correction method of Hayakawa *et al.* (1977) was used to correct heating time in 208 × 006 cans (thermal death time cans). D-values were determined as the time in minutes to reach 150g puncture force. The k_{121} and the E_a values for the beans under the three soaking conditions are presented in Table 4. Quast and Da Silva (1977) reported a similar E_a value (35.5 kcal/mole) for thermal softening of black beans (*Phaseolus vulgaris*) soaked in tap water. The firmness was measured with a Kramer shear press. They also reported E_a values of 37.5 kcal/mole, 43.5 kcal/mole, and 42.2 kcal/mole for brown beans (*Phaseolus vulgaris*), soybeans (*Glycine max*), and Alaska dried peas (*Pisum staivum*), respectively. Sefa-Dedeh *et al.* (1978) found first order kinetics for the softening of cowpeas (*Vigna unguiculata*) heated at 100 °C.

Table 4. Softening of canned black beans[a]

Treatment	k_{121} (min^{-1})	E_a (kcal/mole)
Untreated	0.057	19.1
Distilled water soak (12 h)	0.978	31.3
Salt solution[b] soak	0.983	38.9

[a]Data of Silva *et al.* (1981a,b)
[b]Solution of 2.5% sodium chloride, 1% sodium tripolyphosphate, 0.75% sodium bicarbonate, 0.25% sodium carbonate; soaking for 12 h.

Thermal Softening of Rice.

Amongst cereals, rice is the staple of millions of people worldwide. Thermal softening of rice has been assessed by measurement of viscosity, compressibility, spreading area between glass plates, and cohesiveness (Pillaiyar and Mohandoss 1982). However, it appears that relatively few studies have been conducted on the kinetics of softening of rice. Suzuki *et al.* (1976) employed compressibility ratio to determine first order rate constant for rice heated over the temperature range of 75 to 150 °C. Arrhenius plots of the softening rate constants (Fig. 3) showed that the slope changed at about 110 °C. At temperatures below 110 °C, the activation energy was about 19 kcal/mole, while above 110 °C it was 8.8 kcal/mole. It was concluded that below 110 °C, the softening rate was limited by the reaction rate of rice components with water, while above 110 °C it was limited by the diffusion of water through the cooked layer to the uncooked core.

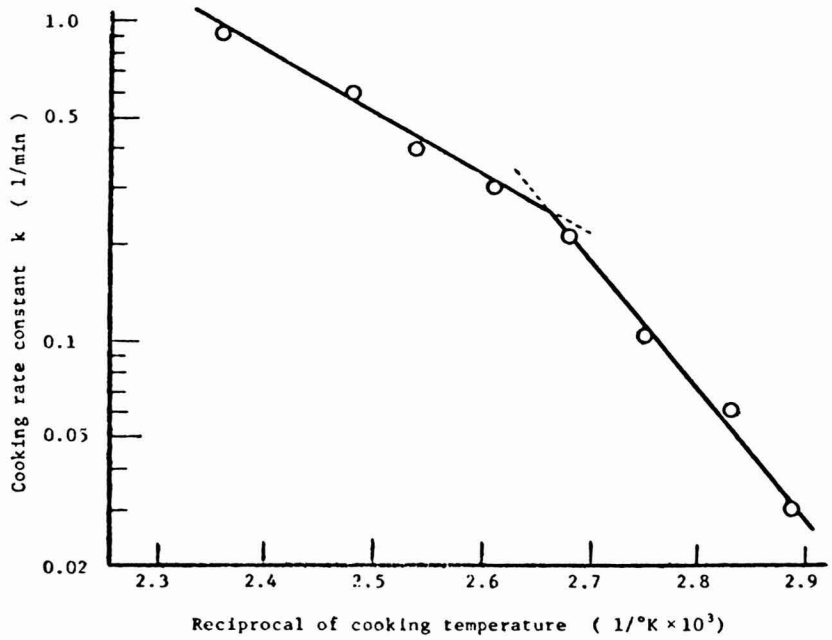

FIG. 3.
ARRHENIUS PLOT FOR SOFTENING OF RICE (source: Suzuki *et al.* 1976)

Thermal Softening of Shrimp

Ma *et al.* (1983) determined kinetic parameters for the texture changes of shrimp in 307 × 113 cans after corrections for thermal lag. Shear force and sensory perception were used to study texture changes. Initially, toughening was observed that was followed by softening (Fig. 4). Heat denaturation of the myofibrillar proteins and shrinkage of collagen experienced in early stages of heat processing are probably responsible for the tightening and stiffening of structure. Softening can be attributed to the conversion of collagen to gelatin and to the dissociation of muscle proteins. For the softening phenomenon, the k_{121} was 0.040 min^{-1} and the magnitude of E_a was 24.5 kcal/mole.

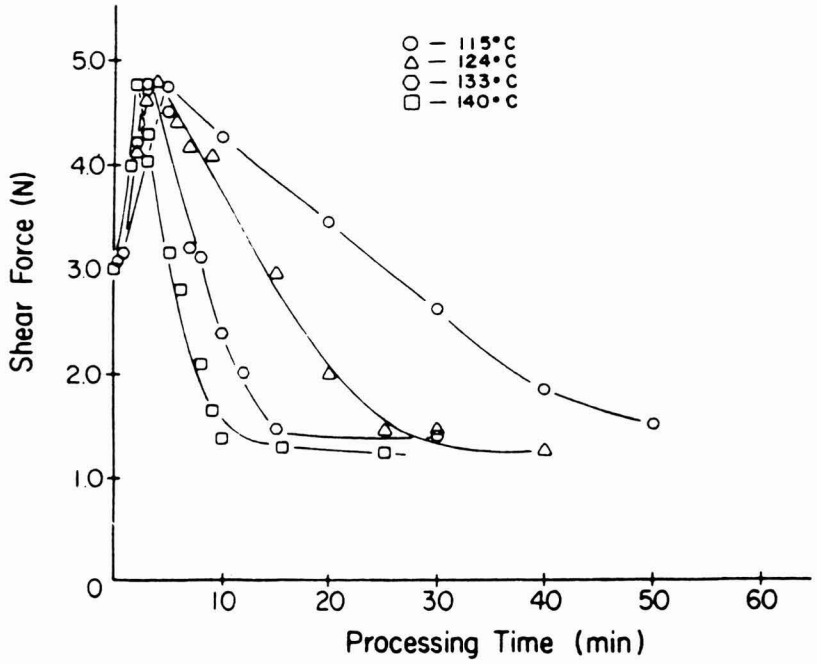

FIG. 4.
TOUGHENING AND SOFTENING OF SHRIMP (source: Ma *et al.* 1983)

Thermal Softening of Meat

The factors affecting tenderness of meat have been discussed earlier. In the discussion it was pointed out that softening is preceded by toughening of meat. It appears that few studies have been dedicated to the determination of kinetic parameters for softening meat. Lund (1982) utilized literature data to calculate activation energies and these are summarized in Table 5.

Table 5. Texture change in meats[a]

Component	pH	Temp., °C	E_a (kcal/mole)
Beef semitendinosus muscle	nat	55–59	140
Kangaroo tail tendon	1.8	50–70	67
	4.2		145
	7.2		152
	12.5		77

[a]Lund (1982)

CONCLUSIONS

Studies on thermal softening of foods indicate that apparent first order kinetic expressions are suitable for expressing the degree of softening at a constant temperature. The effect of temperature on softening can be expressed by Arrhenius relationship. Data are needed on the thermal softening of many foods such as cereals other than rice and poultry meats. It is emphasized that studies must take into consideration the effects of thermal lag and of averaging over the total volume of a container.

Studies are needed on understanding the effect of heat on the tissue of foods. In this respect, techniques such as scanning electron microscopy can provide valuable information.

Studies also are needed on the texture changes in foods during storage. Bourne (1982b) found that for many fruits and vegetables the firmness – temperature relationship was approximately linear. This suggests that the mechanisms for texture changes at low temperatures are different than those at high temperatures. With the exception of the mechanism for softening of beans these mechanisms have not been studied extensively.

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MICRO-COMPUTER PROGRAM FOR DETERMINING THE UNIQUE TIME-TEMPERATURE ASSOCIATED WITH THE EQUIVALENT POINT METHOD OF THERMAL EVALUATION[1]

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INTRODUCTION

The equivalent point method for thermal evaluation was originally proposed for comparing direct and indirect heating aseptic systems being concerned only with constituent changes definable with first order kinetics (Swartzel 1982). More recently, the method has been described as being useful for generating kinetic data (any reaction order) during continuous flow (Swartzel 1984; Swartzel and Jones 1985). With accurate thermal histories the method promises to provide a means to compare all thermal treatments by way of the unique one time and one temperature generated for each thermal curve, independent of activation energies (Swartzel 1986). This method, in spite of simplicity, requires repeated numerical calculations, presenting a suitable problem for a micro-computer to solve. This work describes the program with an example problem.

COMPUTER PROGRAM

The computer program presented in this paper has been developed on an Apple® Macintosh™ computer using Microsoft™ BASIC. The same program with no modifications can be used on an IBM® -pc™. The notations used in the program are either defined in the program or by Swartzel (1982). Figure 1 is a flowchart presentation of the program. Table 1 presents sample input and output values with Fig. 2 showing the time-temperature lines.

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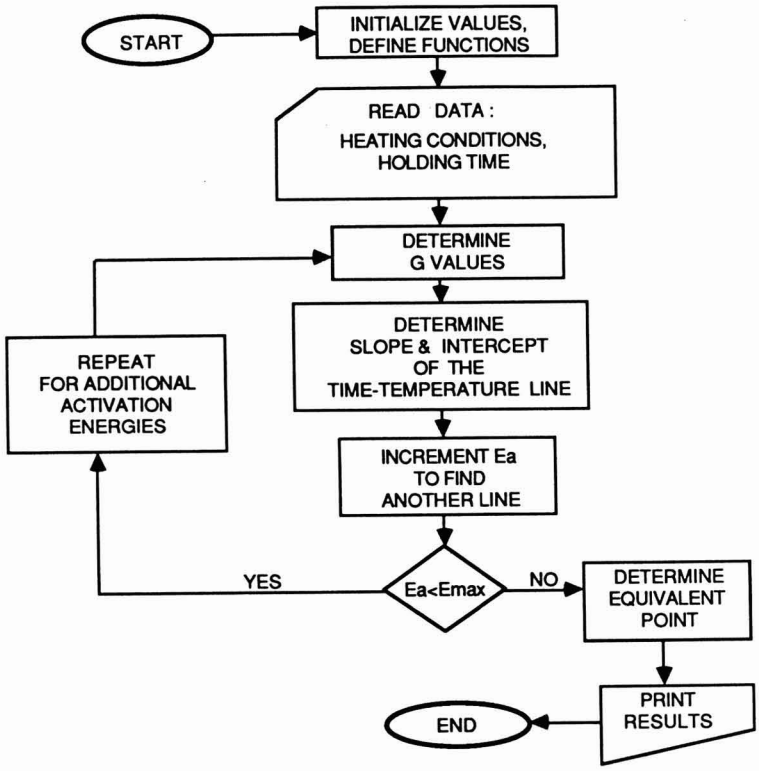

FIG. 1. FLOWCHART FOR COMPUTING EQUIVALENT TIME AND TEMPERATURE FROM DEFINED THERMAL HISTORY

COMMENT

The lines in Fig. 2 do not intersect at an exact point. We attribute this to the accumulated errors associated with the empirical expressions used for determining the exponential integrals and rounding off errors. These errors were not random. As the EA values associated with two intersecting lines increase the determined equivalent time becomes less and the equivalent temperature becomes greater. The computer program presented uses the average value of all the intersections as the best estimate of the equivalent point. The largest Ea/RT value limit usable on most microcomputers is about 96.6 (approximately Ea=300 kJ/mol). If an

EQUIVALENT POINT PROGRAM

```
REM ************************************************************************
REM *      PROGRAM TO CALCULATE EQUIVALENT PROCESS TIME AND                 *
REM *      TEMPERATURES FROM DEFINED THERMAL CURVES.                        *
REM ************************************************************************
DIM  z(4),Te(15,15),Sh(15,15),SLOPE(15),INTERCEPT(15)
PRINT "Enter option number and push return"
PRINT "1) J value is known " : PRINT "2) Temperature pattern is known " : INPUT Opt
REM Initialize constants for the exponential integrals (Abramowitz and Stegun, 1964)
a0=-.5772: a1=1: a2=-.2499: a3=.0552: a4=-.00976: a5=.00108 :b1=8.573: b2=18.06: b3=8.6348: b4=.2678
c1=9.573: c2=25.633: c3=21.1: c4=3.9585
count=0  :  ETemp=0  :   Etime=0  'Initialize values
R=8.314  : Ea=150000! :  Einc=10000! :  Emax=300000! ' Joules/Mol/K and Joules/Mol
DEF FNE1(x)=a0+x*(a1+x*(a2+x*(a3+x*(a4+x*a5))))-LOG(x) 'Exponential integral for 0<x<1
DEF FNEa(x)=(b4+x*(b3+x*(b2+x*(b1+x))))*EXP(-x)
DEF FNEb(x)=(c4+x*(c3+x*(c2+x*(c1+x))))*x
DEF FNE2(x)=FNEa(x)/FNEb(x) 'Exponential function for x>=1
IF Opt=1 THEN GOSUB 1000
HldTemp=MedTemp+(InTemp - MedTemp)*EXP(- j*HeatTim) 'Determine Holding Temperature
IF Opt=2 THEN GOSUB 2000
b=(InTemp-MedTemp)/MedTemp 'Dimensionless Temperature Variable (Swartzel, 1982)
WHILE (Ea<=Emax) AND (Ea<=R*96.6*InTemp)
  REM The value "96.6" is approximately the highest value for the exponent Exp(x).
   REM For other computers this value must be changed according to the accuracy of the computer.
    count=count+1 'Counter to determine number of iterations
    Rr=Ea/R/MedTemp
      x=Ea/R/InTemp : IF (x<1) THEN z(1)=FNE1(x) ELSE z(1)=FNE2(x)
      x1=Rr/(1+b*EXP(- j*HeatTim)) : IF (x1<1) THEN z(2)=FNE1(x1) ELSE z(2)=FNE2(x1)
      x2=x- Rr : IF (x2<1) THEN z(3)=FNE1(x2) ELSE z(3)=FNE2(x2)
      x3=x1- Rr : IF (x3<1) THEN z(4)=FNE1(x3) ELSE z(4)=FNE2(x3)
   Gh=((z(1) - z(2)) - EXP(- Rr)*(z(3) - z(4)))/j 'Heating effect due to the heating section
   Go=EXP(- Ea/R/HldTemp)*HldTime 'Heating effect due to the holding section
   Gt=Gh+Go 'Total heating effect
   REM The following loop computes data for plot of 1/T vs Log(t)
   FOR t=(HeatTim+HldTime)/2 TO 2*(HeatTim+HldTime) STEP (HeatTim+HldTime)/2
     Tp= - Ea/R/LOG(Gt/t)   :    Tr=1/Tp  :  PRINT t,Tp  :  NEXT t
  SLOPE(count)=Ea/R   :     INTERCEPT(count)=LOG(Gt) : ON ERROR GOTO 4000
 Ea=Ea+Einc 'Use another activation energy to determine intercept
WEND
FOR i=1 TO count  :  FOR l=i+1 TO count 'Loop to determine intercepts
  Te(i,l)=(SLOPE(i) - SLOPE(l))/(INTERCEPT(l) - INTERCEPT(i))
   Sh(i,l)=EXP((SLOPE(l)/Te(i,l)+INTERCEPT(l))) : NEXT l  :  NEXT i
FOR i=1 TO count  :  FOR l=i+1 TO count :  ETemp=ETemp+Te(i,l)  :  Etime=Etime+Sh(i,l)  : NEXT l  :  NEXT i
Points=count*(count - 1)/2 :  ETemp=ETemp/Points :  Etime=Etime/Points 'Equivalent Temp.(K), and Time(sec).
PRINT:PRINT TAB(20);"J Value       ",j :  PRINT TAB(20);"Heating Time  ",HeatTim;"sec."
PRINT TAB(20);"Holding Time  ",HldTime;"sec." :  PRINT TAB(20);"Media Temperature",MedTemp - 273;"C"
PRINT TAB(20);"Initial Temperature ",InTemp - 273;"C" :PRINT
PRINT USING "              Holding Temperature ######.# ";HldTemp - 273;:PRINT "C"
PRINT TAB(20);"Number of  t - T   Lines  ",count
PRINT TAB(20);"Number of intercepts ",count*(count - 1)/2
PRINT USING "              EQUIVALENT TIME   #####.#  ";Etime;:PRINT "sec."
PRINT USING"            EQUIVALENT TEMPERATURE   ####.# ";ETemp - 273;:PRINT "C"   :   END
1000 :INPUT "J Value ";j  ' Slope of the heating curve (Swartzel, 1982)
      INPUT "Heating Time in seconds ";HeatTim  : INPUT "Holding time (sec.)"; HldTime
      INPUT "Media Temperature in Degrees C ";MedTemp: MedTemp=MedTemp+273
      INPUT "Product Inlet Temperature in Degrees C ";InTemp
       InTemp=InTemp+273 :  RETURN
2000 : DIM temp(20), Ltemp(20),htime(20)
     ss1=0  :  ss2=0  :  sltemp=0  :  stime=0
     INPUT "How many Thermocouples in the heat exchanger (20 max)";n
      FOR i=1 TO n : PRINT "Enter heating temperature, time";i;:INPUT temp(i),htime(i)
        temp(i)=temp(i)+273 :  NEXT i
      INPUT "Enter heating media Temperature (C)";MedTemp
     MedTemp=MedTemp+273 :  InTemp=temp(1)
     FOR i=1 TO n :   Ltemp(i)=LOG(MedTemp-temp(i)) : sltemp=sltemp+Ltemp(i) :  stime=stime+htime(i) :  NEXT i
        mlt=sltemp/n : mt=stime/n
    FOR i=1 TO n : ss1=ss1+(htime(i)-mt)*(Ltemp(i)-mlt) :  ss2=ss2+(htime(i)-mt)*(htime(i)-mt) : NEXT i: j=-ss1/ss2
     HeatTim=htime(n) : HldTemp=temp(n)
      INPUT "Enter holding time";HldTime : RETURN
4000 : PRINT "The combination of j and time-temperature values cause"
       PRINT "overflow. Please, restart the program with proper values."
       END : RETURN
```

Table 1. Sample Input and Output Values

Input values	J Value	0.23
	Heating Time	8.6 sec.
	Holding Time	5.0 sec.
	Media Temperature	150 C
	Initial Temperature	100 C
Output Values	Holding Temperature	143.1 C
	Number of t-T Lines	15
	Number of intercepts	105
	EQUIVALENT TIME	9.3 sec.
	EQUIVALENT TEMPERATURE	141.6 C

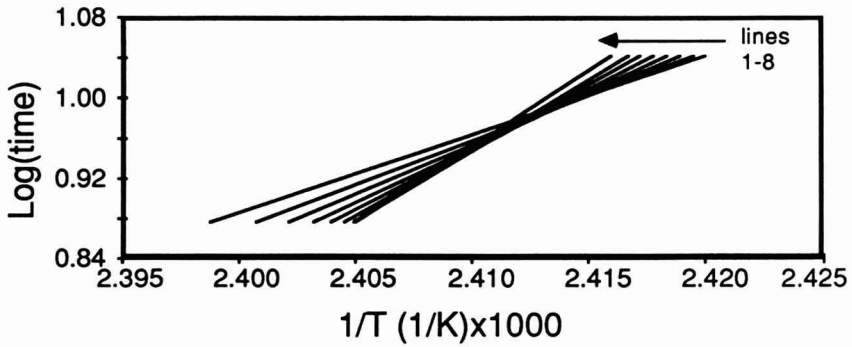

FIG. 2. PLOT OF THE INVERSE OF ABSOLUTE TEMPERATURE VS LOGARITHM OF TIME FOR DIFFERENT ACTIVATION ENERGIES TO DETERMINE THE EQUIVALENT POINT. Only 8 (out of 15) of the activation energies used by the program are shown here for clarity. The first line has an Ea of 150 kJ/mol; second, 170 kJ/mol, etc.

even distribution of Ea values were used, extending into the very low energies, the mean equivalent point would be weighted, indicating larger equivalent time and smaller equivalent temperature than would actually exist. To prevent excessive deviation from the best possible point a narrow mid-range of activation energies were selected for this program. Since this range lies in the middle of Ea values of interest in biological fluid processing, the best non-weighted point would be determined. If this range is used with all thermal evaluations, any associated error of equivalent point determination would in effect become a base line error common to all evaluations.

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HASSON, E. P. and LATIES, G. G. 1976. Separation and characterization of potato lipid acylhydrolases. Plant Physiol. *57*, 142–147.

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