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OSMOTIC DEHYDRATION OF FRUIT: PART 1. SUGARS EXCHANGE BETWEEN FRUIT AND EXTRACTING SYRUPS[1]

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ABSTRACT

The exchange of sugar components in cherry, apricot and peach with the osmotic syrup during osmotic dehydration was analyzed.

Sugar exchange dynamics between the syrup and the fruits was found to be related not only to the flux of sugars from the syrup into the fruit, but is affected also by the individual sugars originally present in the fruit. The exchange is also dependent on the species of fruit, the relative diffusivity of the sugars and enzymatic activity within the fruit.

INTRODUCTION

Osmotic dehydration has recently received attention as an intermediate step in drying, dehydrofreezing and freeze-drying fruits (Ponting *et al.* 1966; Paer and Richberg 1968; Farkas and Lazar 1969; Hope and Vitale 1972; Ponting 1973; Garcia *et al.* 1974; Bongirwar and Sreenivasan 1977; Lerici *et al.* 1977; Hawkes and Flink 1978; Moy *et al.* 1978; Andreotti *et al.* 1983).

Since the method is based on removing only a part of the natural water content of fruits, most previous studies have focussed attention on rapid and effective removal of desired amounts of water. The parameters studied were temperature and pressure (Ponting *et al.* 1966; Farkas and Lazar 1969; Ponting 1973; Dalla Rosa *et al.* 1982), concentration and composition of extracting syrup (Ponting *et al.* 1966; Ponting 1973; Hawkes and Flink 1978; Andreotti *et al.* 1983; Bolin *et al.* 1983) and chemical pretreatment (Camirand *et al.* 1968; Paer and Richberg 1968; Garcia *et al.* 1974; Dymsza 1975).

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Recently osmotic dehydration was used to obtain high water-activity fruit products (a_W 0.94–0.97) which, after vacuum-packaging and pasteurization, remained stable for many months at ambient temperature (Maltini and Torreggiani 1981; Maltini *et al.* 1983). This process causes minimal changes on the sensory and physical-chemical characteristics of fruits.

Theoretical studies carried out by Hawkes and Flink (1978) identified solids gain due to the penetration of soluble substance from the osmotic medium into the fruit and the mass transport coefficient, as significant factors affecting water removal and quality of the osmotic dehydrated product.

Some data are available on solids penetration into osmodehydrated fruits. However, all of the data were based on total solids gain, assuming that the solutes initially present in the fruit do not diffuse into the much more concentrate osmotic medium. Dixon and Jen (1977) studied sugar exchange in osmodehydrated apples and concluded that solids in the fruit increased or remained at the initial level.

The present study was carried out to determine the influence of type and concentration of sugars both in the fruit and in the syrup on sugars exchange by separately accounting for each sugar naturally present in the fruit and those present in the osmotic syrup.

MATERIALS AND METHODS

Raw Material

The following fruits were used: cherries ("Bianca di Verona" cultivar), apricots ("Reale" cultivar) and clingstone peaches ("Baby Gold 6" cultivar), harvested at a maturation stage suitable for processing.

Fruits were trimmed. Cherries (average diameter 1.8 cm) were stemmed and pitted, apricots were stoned and cut into ca. 1 cm thick halves, peaches were lye-peeled (7% NaOH at 80 °C for 40 s), stoned and cut into ca. 2 cm thick slices.

Osmotic Syrup

A 50%(w/w) corn syrup/sucrose blend at 70 °Bx was used in cherries and peaches. Corn syrup had a composition as follows: glucose 24%, maltose 29%, polysaccharides 12%, water 35%. A sucrose syrup at 70 °Bx and a syrup consisting of a mixture of fructose, glucose and sucrose at 65.2 °Bx were used in apricots. Ascorbic acid (1%) was added as an antioxidant to all the syrups.

Process

The fruits were allowed to contact the syrups at ambient temperature (ca. 25 °C) for 6 h. Samples were removed at ½, 1, 2, 4, 6 h. The syrup was con-

tinuously recirculated using a peristaltic pump. The fruit/syrup ratio was constant at 1:5 (w/w). Syrup was sampled at the same time as the fruit. To simplify sampling, the fruits were contained in preweighed numbered baskets. Baskets were removed individually, sprayed with water to remove the adhering syrup, dripped and weighed. Each experiment was repeated twice.

Dehydration Parameters

Total solids were determined in a vacuum oven at 60 °C for 24 h. Following Hawkes and Flink (1978), these parameters were calculated: water loss

$$WL = \frac{(ww_0)-(tw-ws)}{(ws_0 + ww_0)} \times 100$$

where ww_0 is the weight of water initially present, ws_0 the initial weight of solids, tw the weight of the fruit at the time of sampling and ws the weight of solids in the fruit at the time of sampling. Solid gain (SG) was calculated as follows:

$$SG = \frac{(ws-ws_0)}{(ws_0 + ww_0)} \times 100$$

NSC, the dimensionless solid content equal to ws/ws_0, was used to calculate the mass transport coefficients K′, using: $NSC = K'(t)^{1/2}$. Data at time 0 were excluded from the analysis.

Sugar Analysis

Sugars were analyzed by HPLC of acqueous extracts of fruit or diluted syrup. A JASCO GP-A 30 chromatograph was used under the following conditions: flow 1.5 mL/min, eluent acetonitril/water 75/25, LiChrosorb NH_2 column (10 μm)(200 × 4 id.mm), refraction index detector SHODEX RI SE 11, recorder-integrator SHIMADZU CHROMATOPAC C-RIB, internal standard 1% methyl-D-glycoside. All reported results are average of the analyses of two samples run in triplicate, with a standard error ranging from 0.02 to 0.05.

Material Balance of Individual Sugars (ΔC)

The difference between the amount of indivdual sugars in the fruit samples in the basket before the treatment (C_0) and that present at a time of sampling (C_t) divided by the initial weight (P_0) was calculated according to:

$$\Delta C = \frac{C_t-C_0}{P_0} \times 100$$

RESULTS AND DISCUSSION

Water loss, dry weight, solid gain and dimensionless solids content of the fruits at various contact times with the indicated syrups are shown in Table 1. These data illustrate the difference in behavior of the three fruits examined. The difference between the data for cherry and peach, treated with the same extracting syrup, seems to involve the intrinsic properties of these two fruits. In addition to the different structure and compactness of the tissues, the size of the contact surface between the fruit and the syrup influence water loss and sugar exchange.

The sliced peeled peach, has the largest surface available for sugar and moisture exchange, while the cherry, with the peel on, exhibited the smallest surface. The surface exchange area difference is manifested by far smaller dehydration rates for cherries compared to peaches. However, there appears to be a small difference in solid gain and normalized solid content between all fruits. Moreover, a 94.6% increase in dry matter occurred in peaches, in comparison with as little as 53.3% increase in cherries. In the case of apricots, the loss of water appears to be dependent on the type of syrup used; with monosaccharides allowing more loss than disaccharide. Total solids content in apricots appears to be parallel in either sugar, even though solid penetration is slightly greater in the presence of fructose and glucose.

The amount of solids that penetrated the fruits in 6 h as shown in Table 1 was different for apricots where about 20% (5.3/26.5) of total solids entered the fruit compared to approximately 5% (1.3–1.4/27–29) in the two other fruits.

To evaluate the interaction between the fruits and the osmotic solutions, the sugar composition in the fruit and syrup phases was determined.

Table 2 shows the fructose, glucose, sucrose and maltose contents in the dry matter of the different fruits. Table 3 shows the percentages of the same sugars in the osmotic syrups used, also calculated on a dry matter basis. First and foremost the sugars in the fruits are a characteristic of the species, in particular there is a lack of sucrose in cherries. As the equilibration time increase, the ratios between the various components showed considerable changes. These ratios changed most in cherries and peaches due to the considerable penetration of maltose from the syrup. The maltose absorption rate is different in the two fruits, because it took six hours for cherries to reach the value that peaches reached after just half an hour's dipping. A selective diffusion seems to take place in the cherry where despite the strong presence of sucrose in the syrup, no penetration of this sugar occurred. Another explanation of the lack of sucrose in cherries could be a strong invertase activity in the fruit. A study on the influence of the cultivar on the dehydration rate and sugar exchange (Torreggiani *et al.* 1986) confirmed that osmodehydrated cherries do not contain sucrose, while an amount of maltose, also a disaccharide, is always present.

TABLE 1.
MASS TRANSPORT DURING OSMOTIC DEHYDRATION OF CHERRIES, PEACHES AND APRICOTS

	CHERRY				PEACH				APRICOT 1 a				APRICOT 2 b			
time hrs	WL	TS	SG	NSC	WL	TS	SG	NSC	WL	TS	SG	NSC	WL	TS	SG	NSC
0		18.76		1.00		13.87		1.00		12.88		1.00		14.86		1.00
1/2	7.12	20.92	0.64	1.11	19.86	17.83	0.49	1.28	7.19	15.89	2.28	1.22	7.38	17.12	1.43	1.15
1	14.39	22.31	0.34	1.19	27.66	20.33	1.07	1.46	11.11	16.89	2.84	1.30	14.59	20.05	3.38	1.35
2	24.51	25.03	0.13	1.33	33.58	22.38	1.21	1.61	17.98	19.32	4.11	1.50	19.85	21.86	4.23	1.47
4	26.64	27.15	1.16	1.48	40.09	24.50	1.07	1.77	27.07	22.88	5.86	1.76	30.21	26.10	6.13	1.76
6	29.82	28.76	1.42	1.53	44.94	26.99	1.32	1.94	30.03	23.16	5.36	1.78	34.38	26.50	5.28	1.78

WL = water loss, TS = total solids, SG = solid gain, NSC = normalized solids content
a - sucrose syrup, b - fructose, glucose, sucrose syrup.

TABLE 2.
CONCENTRATION OF INDIVIDUAL SUGARS IN THE FRUITS (g sugar/100 g dry matter), DURING THE OSMOTIC PROCESS

	CHERRY				PEACH				APRICOT 1				APRICOT 2			
time hrs	F	G	S	M	F	G	S	M	F	G	S	M	F	G	S	M
0	22.26	44.60	-	-	10.38	12.25	50.48	-	6.08	10.73	26.62	-	9.02	24.10	24.09	-
1/2	21.72	47.62	-	-	7.97	17.03	46.08	5.55	5.40	9.97	30.10	-	15.46	25.48	24.34	-
1	22.13	48.34	-	1.90	7.70	17.65	44.50	6.25	5.07	9.68	36.30	-	18.83	29.17	27.78	-
2	19.93	44.83	-	2.81	7.29	17.25	42.05	7.21	5.24	9.37	39.56	-	19.02	30.17	25.19	-
4	20.62	44.78	-	2.93	6.88	17.78	41.49	7.80	4.72	8.94	41.63	-	21.36	33.01	22.39	-
6	20.07	43.66	-	4.76	6.59	17.99	41.54	8.12	4.08	8.81	41.82	-	19.92	31.41	23.52	-

F = fructose; G = glucose; S = sucrose; M = maltose.

TABLE 3.
CONCENTRATION OF SUGARS IN THE OSMOTIC SYRUPS (g sugar/100 g dry matter), DURING THE OSMOTIC PROCESS

	CHERRY				PEACH				APRICOT 1				APRICOT 2			
time hrs	F	G	S	M	F	G	S	M	F	G	S	M	F	G	S	M
0	2.30	23.05	34.60	21.30	2.50	25.12	35.39	26.81	-	-	94.91	-	37.79	46.09	14.05	-
1/2	2.37	22.91	34.56	21.21	2.72	24.97	36.07	25.56	-	-	89.48	-	37.59	43.39	12.42	-
1	2.00	22.04	34.73	21.12	2.60	24.84	36.67	23.18	-	-	90.13	-	36.01	41.26	12.10	-
2	2.10	21.60	34.69	20.10	2.76	25.49	37.12	22.87	-	-	90.28	-	35.37	40.27	11.39	-
4	2.14	21.45	34.73	19.60	2.64	25.41	37.08	22.70	-	0.71	88.38	-	35.50	40.87	11.57	-
6	2.23	22.61	34.76	17.92	2.47	24.52	38.12	22.87	0.59	1.04	84.82	-	35.29	39.71	10.73	-

F = fructose; G = glucose; S = sucrose; M = maltose.

The changes in the ratios between fructose, glucose and sucrose in apricots treated only with sucrose gave initial values of 1:2.5:4.4 and 1:4.7:10.2 after six hours of osmosis. This change combines the effect of a predictable gain in sucrose, which showed considerable penetration, and glucose uptake, even though glucose is not initially present in the syrup. When syrup containing fructose, glucose and sucrose was used the starting ratio of 1:2.7:2.7 became 1:1.6:1.3 after 6 h, showing that fructose gain was greater than glucose. The quantitative migrations of each sugar may be obtained by the material balance of individual sugar (ΔC), reported in Fig. 1 as a percentage of the initial value. Figure 2 shows the regression lines calculated from the ΔC data as a function of time (expressed as $\sqrt{t}$ only for graphical reasons) for cherry and peach.

In cherries, fructose and glucose showed a marked tendency to leach out of the fruit after an initial glucose gain.

In peaches the phenomenon is much more complex. According to the laws of osmosis, the peach should be penetrated by all the sugars in the syrup since the concentration is higher in the syrup than it is in the fruit. The analyses showed however, that sucrose in the fruit decreased from the initial concentration. It appears that both the original sucrose and that penetrated from the syrup are hydrolyzed during the equilibration process. Thus the glucose in the fruit increased because of penetration from the syrup and sucrose hydrolysis. Fructose content, notwithstanding hydrolysis, showed a decreasing trend. A possible explanation for this phenomenon is that the fructose from sucrose hydrolysis is leached out of the fruit.

In Fig. 3 the regression lines calculated from the ΔC data as a function of time for apricots are shown.

Apricots treated only with sucrose in the syrup will allow only the penetration of the latter sugar in the fruit. Sucrose concentration tended to increase in the fruit. At the same time, however, fructose content was relatively constant and the uptake of glucose was very slight. This bears out the hypothesis that part of the sucrose that penetrated the fruit is hydrolyzed and that, of the two monosaccharides, fructose comes out as it is formed by hydrolysis. Glucose comes out more slowly, therefore a slightly upward sloping curve was exhibited. The hypothesis that sucrose hydrolyzes very rapidly in apricots is confirmed by data from storage of these products (unpublished). As early as 24 days of storage at 0 °C only traces of sucrose were present, while the two monosaccharides were present in stoichiometric quantities.

When apricots were treated with a syrup containing mixed sugars an increase in each sugar was observed. Hydrolysis of sucrose that penetrated the fruit cannot be ascertained, since the two monosaccharides present in the syrup will also penetrate the fruit. For this reason the amount of monosaccharides in the fruit that is formed by hydrolysis cannot be distinguished from those that diffused into the fruit.

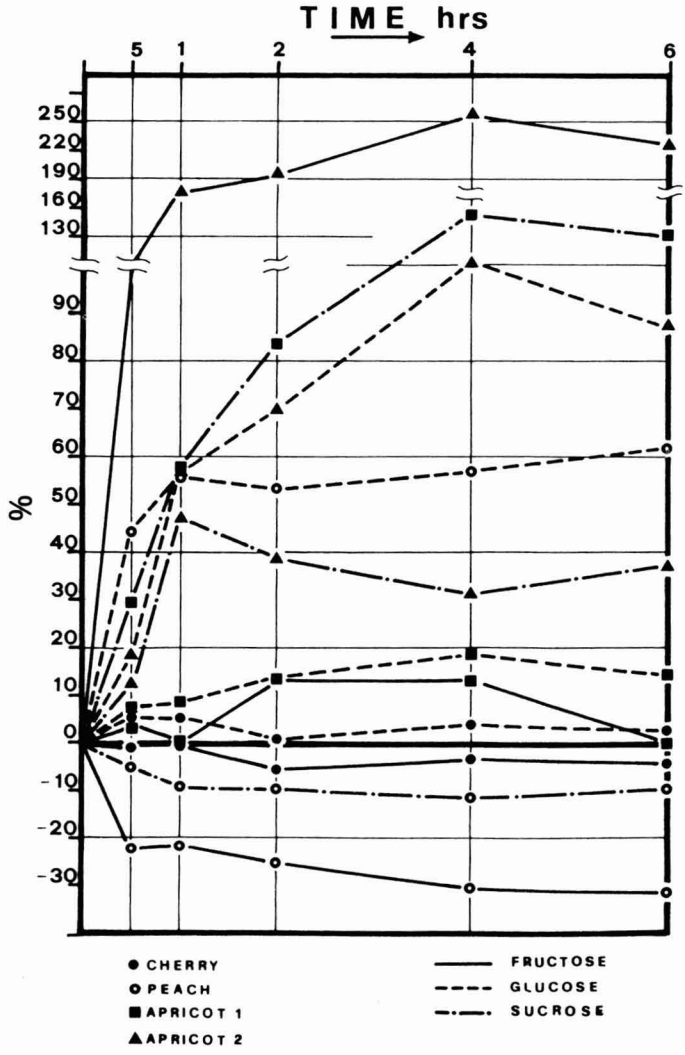

FIG. 1. CHANGE IN INDIVIDUAL SUGARS CALCULATED AS PERCENTAGE OF INITIAL CONCENTRATION DURING THE OSMOTIC PROCESS:
F = fructose; G = glucose; S = sucrose.

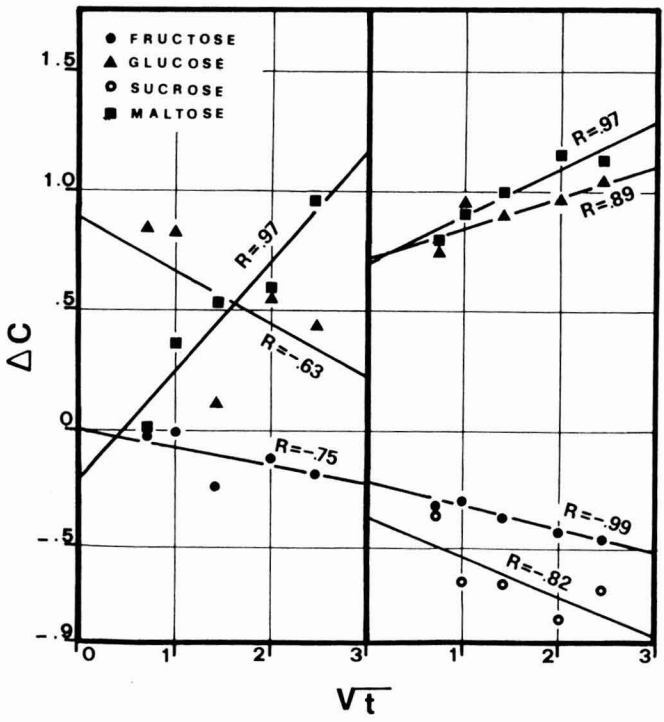

FIG. 2. CHANGE IN CONCENTRATION OF INDIVIDUAL SUGARS (△C) DURING THE OSMOTIC PROCESS FOR CHERRY (LEFT) AND PEACH (RIGHT)

CONCLUSIONS

The results reported here emphasize the fact that the dynamics of sugar exchange between the syrup and fruit during osmotic dehydration is not only related to diffusion but is a complex process involving the original sugars in the fruit and enzymatic activity. The equations used to calculate solid gain and mass transport rates describe only the net exchange in each product. Thus only the change in total solids can be adequately modelled.

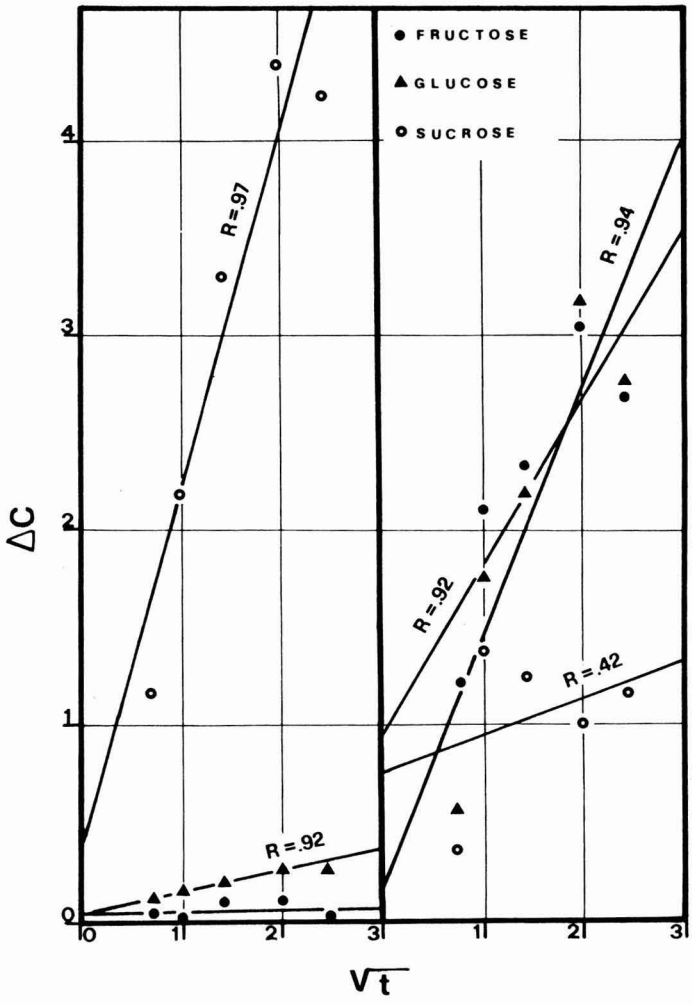

FIG. 3. CHANGE IN CONCENTRATION OF INDIVIDUAL SUGARS (△C) DURING THE OSMOTIC PROCESS FOR APRICOTS USING A SUCROSE SYRUP (LEFT) AND A MIXTURE OF SUGARS (RIGHT)

In some cases where osmotic dehydration is used as a pretreatment for further operations, a change in the ratios of the sugars contained in the fruits can be desirable. The sugar composition of extracting syrups can be selected relative to the sugars already in the fruit. And when the sugar permeability of the fruits is considered, a desirable sugar mix in the products can be obtained. Attention must also be focused on the frequently observed hydrolysis of sucrose during the osmotic dehydration process.

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A KINETIC MODEL FOR OXIDATION OF ASCORBIC ACID AND BETA-CAROTENE

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ABSTRACT

A kinetic model of ascorbic acid oxidation in an aqueous solution, in which dissolved oxygen concentration is held constant, was developed. The model consists of consecutive reactions, $A \xrightarrow{k_A} B \xrightarrow{k_B} C$, where A is ascorbic acid, B is an intermediate, C is an oxidized product, k_A is a zero-order rate constant with respect to ascorbic acid concentration, k_B is a first-order rate constant with respect to intermediate concentration. When it was assumed that A and B gave the same response to chemical determination of A, the model fitted the observation well. The model shows that it is possible for the time course of the reaction to have either first- or zero-order feature in accordance with initial concentrations of A and the ratios of k_A to k_B. In addition, it was also used for the description of beta-carotene degradation.

INTRODUCTION

Ascorbic acid is one of the most labile components in foods and has been used as a quality index, for example, in the prediction of shelf-life of dehydrated foods (Waletzko and Labuza 1976; Riemer and Karel 1977; Singh *et al.* 1983). Then many works have been done on kinetics of ascorbic acid oxidation. Some of the results have shown that the reaction follows a zero-order kinetics with respect to ascorbic acid concentration (Barron *et al.* 1936; Karel and Nickerson 1964; Laing *et al.* 1978). Some authors have described the oxidation behaves as a first-order reaction with respect to ascorbic acid concentration (Deng *et al.*

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1978; Dennison and Kirk 1982; Eison-Perchonok and Downes 1982; Singh *et al.* 1983). Davidson and Grieger-Block (1977) have shown that observed kinetics of ascorbic acid oxidation is affected by interaction between oxygen transfer and chemical reaction. In the present experiment, the reaction behaved as a first-order reaction or as a zero-order reaction with respect to ascorbic acid concentration depending on the conditions even in aqueous solution containing dissolved oxygen of constant concentration and no catalyst. Furthermore, a change in the first-order rate constants with time and a dependence of the constants on initial concentration of ascorbic acid have been observed in the ascorbic acid-dissolved oxygen-copper catalyst systems and in the foods (Dekker and Dickinson 1940; Silverblatt *et al.* 1943; Ogata *et al.* 1968; Deng *et al.* 1978). Our experiment showed that, when the data analyzed as a first-order reaction with respect to ascorbic acid concentration, they deviated from the straight line in the early stage of the reaction. The similar observation has been recorded in beta-carotene oxidation (Stefanovich and Karel 1982).

The present work attempts to find a kinetic model which accounts for a drift of the rate constants with respect to ascorbic acid concentration during time course, for a dependence of the constants on initial ascorbic acid concentration, and for a fact that the oxidation behaves as a first-order reaction with respect to ascorbic acid concentration at one time and as a zero-order reaction with respect to ascorbic acid concentration at another time.

MATERIALS AND METHODS

Ascorbic Acid

Crystalline ascorbic acid was used as received. The purity of 99.7% was made certain by the iodometric titration (Koseisho 1981).

Procedure

Purified water (Japanese Pharmacopoeia) was saturated with air, oxygen, or 10% oxygen-90% nitrogen mixture by continuous aeration at a fixed temperature. Dissolved oxygen concentration was monitored by an oxygen electrode. After the response of the electrode reached a plateau, the concentration of dissolved oxygen was determined by the Winkler titration (Magara 1973), ascorbic acid was dissolved in a fraction of the gas-saturated water, and the solution was added into the bulk of the water. At that time, sample was drawn, ascorbic acid in the sample was determined, and the value was taken as the observed initial concentration. After that, aeration into the solution by water-saturated gas was continued and the determinations of ascorbic acid in samples drawn at adequate intervals were undertaken. Continuous monitoring by the electrode made

certain that the dissolved oxygen concentration remained constant throughout the experimental period. All of the instruments with which the ascorbic acid solution contacted were prepared from glassware to avoid catalytic action of metal walls.

Analysis

Ascorbic acid was determined by HPLC method (Miki 1981), using Finepak Sil C_{18}-10 column (4.6(i.d.)×250 mm) and 0.1% phosphoric acid as eluent. The method was not affected by dehydroascorbic acid.

Data on Beta-Carotene Oxidation

The data recorded in Fig. 1 in the article by Stefanovich and Karel (1982) were used.

RESULTS AND DISCUSSION

Reaction Model

Aqueous ascorbic acid solution of 266 mg/L was continuously aerated by air at 30 °C. The decreasing rates of the acid concentration were determined from a plot of concentration against time and logarithm of rate was plotted against logarithm of concentration (Fig. 1). The figure shows that the reaction is not of a simple order except in an advanced stage of the reaction. That is why we tested the following reaction model.

The following assumptions were made to build the model.

(1) Ascorbic acid, A, converts to an oxidation product through an intermediate, B.
(2) In the reaction, the first step is a zero-order reaction with respect to the concentration of A and the second is a first-order reaction with respect to the concentration of B.
(3) The chemical analysis used can not distinguish between A and B, then determined concentration of A, [A], includes concentration of A and B, [A] and [B].

When t is a reaction time, these lead to the following equations:

$$\text{When } t \leq [A]_O/k_A, \quad [A\,'] = [A] + [B] = [A]_O - k_A t + (k_A/k_B)(1-\exp(-k_B t)) \quad (1)$$

when $t > [A]_O/k_A$, since all of A has disappeared,

$$[A\,'] = [B] = (k_A/k_B)(1-\exp(-k_B[A]_O/k_A)\cdot\exp(-k_B(t-([A]_O/k_A))) \quad (2)$$

where $[A]_O$ = an initial concentration of ascorbic acid, k_A = a zero-order rate constant with respect to ascorbic acid concentration, and k_B = a first-order rate constant with respect to intermediate concentration.

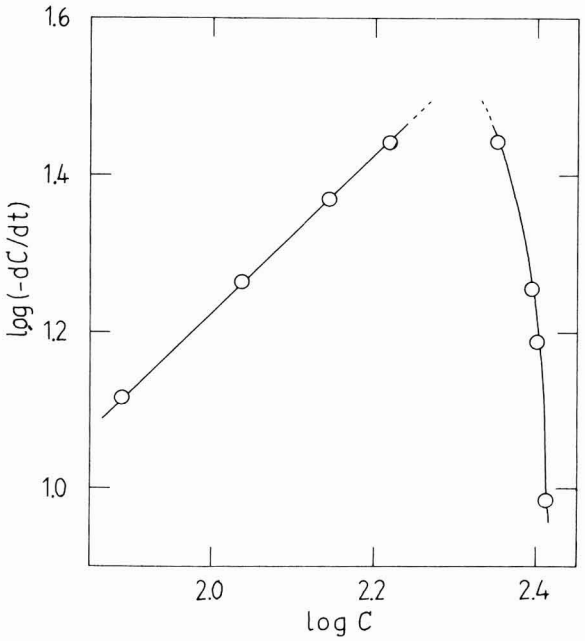

FIG. 1. LOGARITHMIC PLOT OF RATE AGAINST CONCENTRATION (C) FOR ASCORBIC ACID OXIDATION IN AQUEOUS SOLUTION CONTINUOUSLY AERATED BY AIR AT 30 °C
○, obtained from the plots of concentration against time.

Ascorbic Acid Oxidation

The time course of oxidation of ascorbic acid (observed $[A]_O$ = 266 mg/L) in aqueous solution continuously aerated by air was monitored at 30 °C. The result is shown in Fig. 2 in which logarithm of ($[A']/[A]_O$) is plotted against time. After a period of time, log ($[A']/[A]_O$) decreased linearly as time progressed. By applying regression analysis (Bauer 1971) to the straight line region of the plots (Eq. 2) and calculating the slope, k_B was found to be 0.169 h^{-1}. When regression analysis was applied to the straight line obtained by plotting [A'] in the curved line region of the plots (Eq. 1) against $t-((1-\exp(-k_Bt))/k_B)$, k_A was found to be 81.3 $mg \cdot L^{-1} \cdot h^{-1}$ and $[A]_O$ was estimated at 264 mg/L. In the figure, the progress of curve obtained by substituting k_A, k_B, and $[A]_O$ estimated in Eq. (1) and (2) is given by the solid line and the dotted lines show the standard deviation calculated from the deviations of the observed values from the calculated line (Bauer 1971). In Fig. 3, the curve obtained by substituting $[A]_O$ = 114 mg/L and the rate constants presented above in Eq. (1) and (2) is compared with the data obtained in oxidation of ascorbic acid of observed $[A]_O$ of 114 mg/L and the result shown in Fig. 2 is added. The figure shows that both of the rate constants are independent of the initial concentration of ascorbic acid. Figure 4 is another example of ascorbic acid oxidation described by the model.

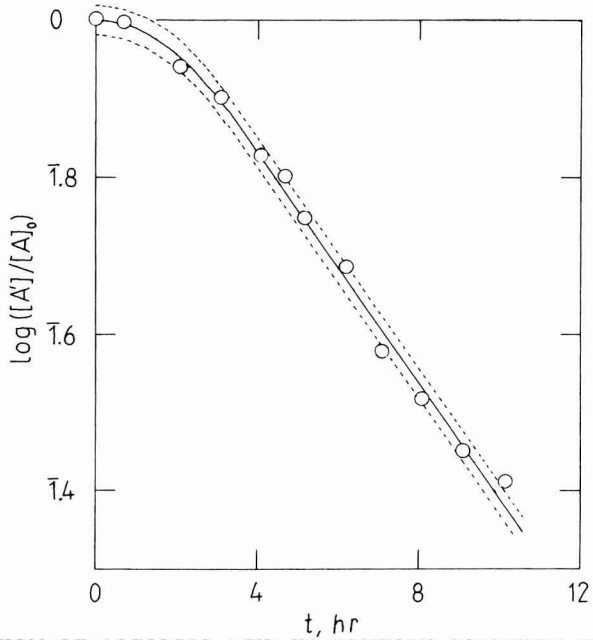

FIG. 2. OXIDATION OF ASCORBIC ACID IN AQUEOUS SOLUTION CONTINUOUSLY AERATED BY AIR AT 30°C

○, obsvd., $[A]_O$=266 mg/L; ——, drawn from $[A]_O$=264 mg/L, k_A=81.3 mg·L^{-1}·h^{-1}, and k_B=0.169 h^{-1} using Eq. (1) and (2); ----, ±(standard deviation).

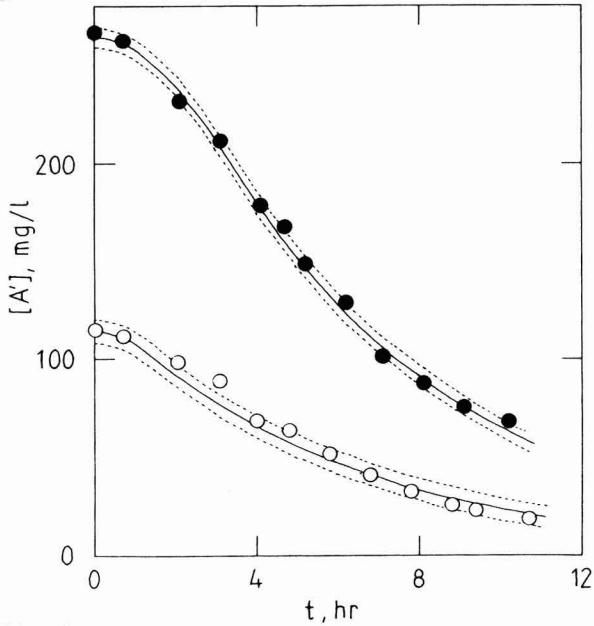

FIG. 3. OXIDATION OF ASCORBIC ACID IN AQUEOUS SOLUTION CONTINUOUSLY AERATED BY AIR AT 30°C

●, obsvd., $[A]_O$=266 mg/L; ○, obsvd., $[A]_O$=114 mg/L; ——, drawn from k_A=81.3 mg·L^{-1}·h^{-1}, k_B=0.169 h^{-1}, and $[A]_O$=264 mg/L (●) or 114 mg/L (○), using Eq. (1) and (2); ----, ±(standard deviation).

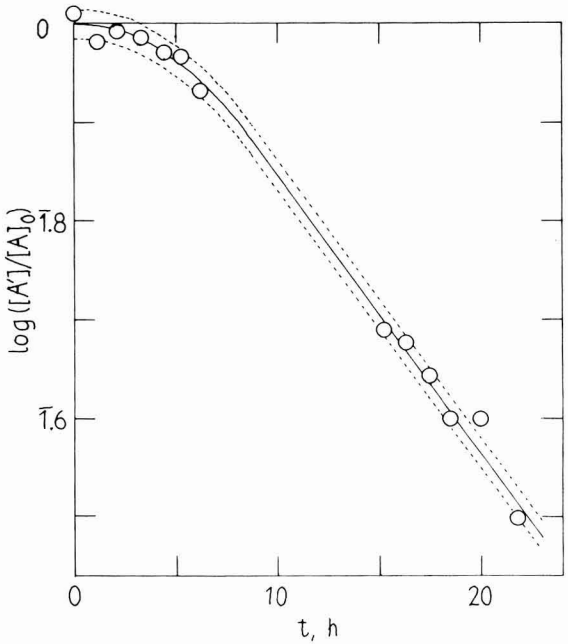

FIG. 4. OXIDATION OF ASCORBIC ACID IN AQUEOUS SOLUTION CONTINUOUSLY AERATED BY 10% OXYGEN-90% NITROGEN AT 31 °C ($[O_2]=130\times10^{-6}$ mol/L)
○, obsvd., $[A]_O=264$ mg/L; ——, drawn from $[A]_O=258$ mg/L, $k_A=29.6$ mg·L^{-1}·h^{-1}, and $k_B=0.0648$ h^{-1} using Eq. (1) and (2).

The application of the present model to the data recorded by Eison-Perchonok and Downes (1982) and by Joslyn and Miller (1949) in the presence of copper catalyst are shown in Fig. 5 and 6, respectively. The figures show that the model is right for their data. However, the rate constants which Eison-Perchonok and Downes recorded in the absence of a copper catalyst are seemingly large as compared with the present data. It is probably attributable to catalytic effects of buffer and of the stainless steel wall of the reaction vessel they used.

Beta-Carotene Oxidation

The model was applied to the results of beta-carotene oxidation recorded by Stefanovich and Karel (1982). Constants k_A and k_B were calculated from the data of the initial concentration of 0.55 mg/g. As shown in Fig. 7, log [A'] against time curve calculated by use of these constants fit well with the data for initial concentrations of 0.85 mg/g and of 0.17 mg/g. The figure shows that the model describes well the progress of oxidation of beta-carotene and the rate constants are independent of the initial concentration. In addition, the figure shows the existence of an induction period which appears when the data are analyzed as a first-order reaction.

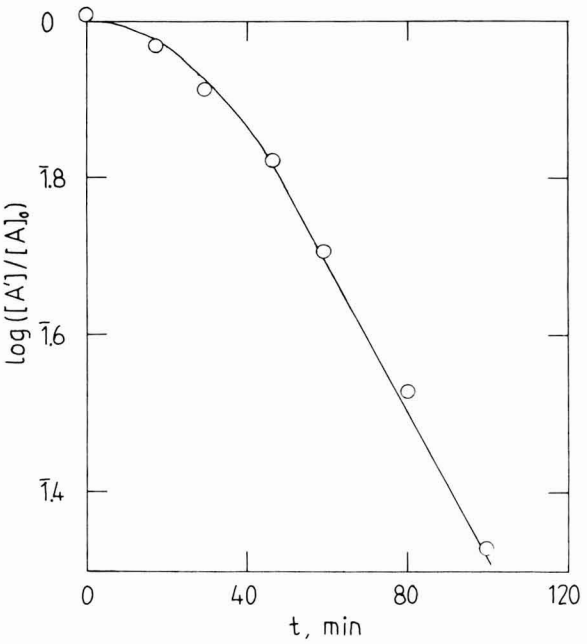

FIG. 5. OXIDATION OF ASCORBIC ACID IN BUFFERED AQUEOUS SOLUTION AERATED BY GAS MIXTURE CONTAINING 21% O_2 AT 40°C[1]

O, data recorded by Eison-Perchonok and Downes (1982), $[A]_O$=464 mg/L; ——, drawn from $[A]_0$=454 mg/L, k_A=9.21 mg·L^{-1}·min^{-1}, and k_B=0.0215 min^{-1} using Eq. (1) and (2).

Diversity of Kinetic Behavior

The present model explains why ascorbic acid oxidation is observed as a first-order reaction at one time and as a zero-order reaction at another time. Figure 8 shows that the reaction looks like a first-order reaction when $k_A \blacktriangleright k_B[A]_O$ and like a zero-order one when $k_A \blacktriangleleft k_B[A]_O$. Examples of the experimental results are shown in Fig. 9. The figure shows that comparative magnitudes of $[A]_O$, k_A, and k_B are able to have an effect on appeared order even in aqueous solution in which dissolved oxygen concentration is kept constant, although Davidson and Grieger-Block (1977) has argued that observed order depends on interaction between oxygen transfer and chemical reaction.

[1]Details of data were given by a private communication from Eison-Perchonok.

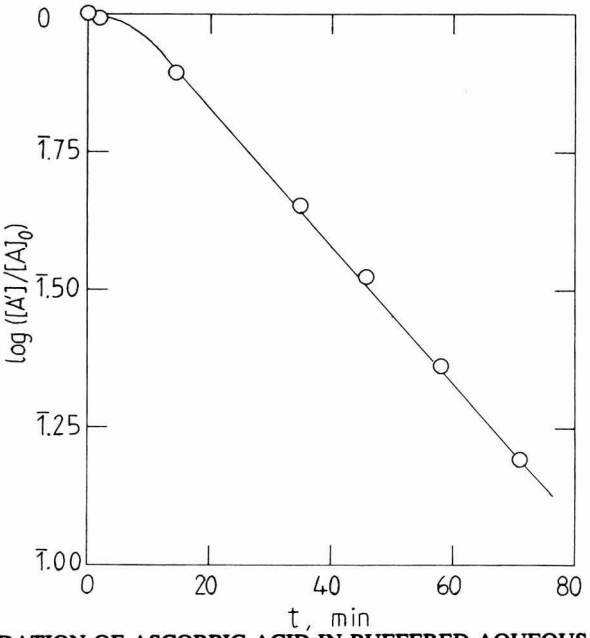

FIG. 6. OXIDATION OF ASCORBIC ACID IN BUFFERED AQUEOUS SOLUTION CONTINUOUSLY AERATED BY OXYGEN IN THE PRESENCE OF 0.54 ppm COPPER AT 30 °F

○, obsvd., $[A]_O$=490 mg/L; ——, drawn from $[A]_O$=485 mg/L, k_A=38.5 mg·L^{-1}·min^{-1}, and k_B=0.0291 min^{-1} using Eq. (1) and (2).

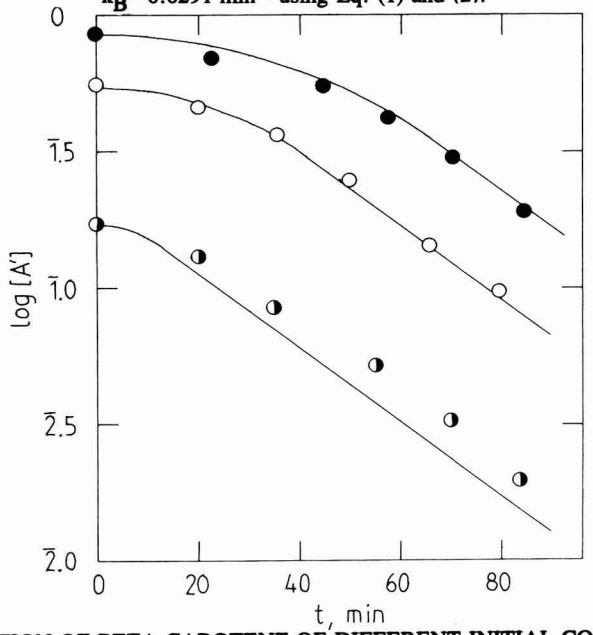

FIG. 7. OXIDATION OF BETA-CAROTENE OF DIFFERENT INITIAL CONCENTRATIONS AT 80 °C REPORTED BY STEFANOVICH AND KAREL (1982)

●, obsvd., $[A]_O$=85 mg/g; ○, obsvd., $[A]_O$=0.55 mg/g; ◑, obsvd., $[A]_O$=0.17 mg/g; ——, drawn from k_A=0.0131 mg·g^{-1}·min^{-1}, k_B=0.0312 min^{-1}, and $[A]_O$=0.85 mg/g (●), 0.54 mg/g (○), or 0.17 mg/g (◑) using Eq. (1) and (2).

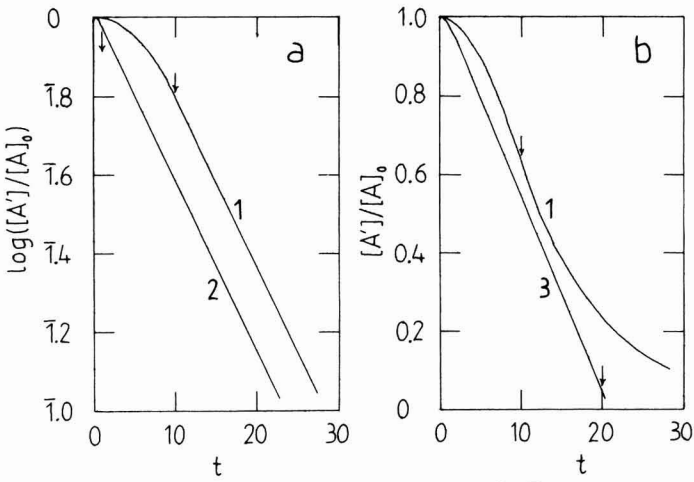

FIG. 8. VARIATIONS WITH $k_A/(k_B[A]_O)$ OF CONCENTRATION AGAINST TIME CURVE 1, $k_A/(k_B[A]_O)=1$; 2, $k_A/(k_B[A]_O)=10$; 3, $k_A/(k_B[A]_O)=0.05$; ↓, time at which all of A has disappeared.

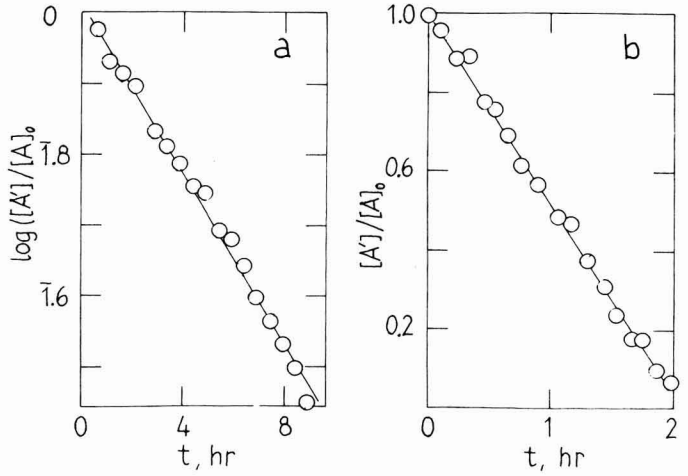

FIG. 9. OXIDATION OF ASCORBIC ACID IN AQUEOUS SOLUTION CONTINUOUSLY AERATED BY OXYGEN AT 30 °C (a) AND AT 71 °C (b)
(a) $[O_2]=1020\times10^{-6}$ mol/L, $[A]_0$ = 168 mg/L, ○, obsvd., ____, linear plot for a first-order reaction; (b) $[O_2]=490\times10^{-6}$ mol/L, $[A]_0$=227 mg/L, ○, obsvd., ——, linear plot for a zero-order reaction.

ACKNOWLEDGMENTS

We thank Dr. Eison-Perchonok who gave us the details in the experimental results in their article.

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EFFECTS OF PRESSURE PROCESSING ON FROZEN STORED MUSCLE PROTEINS OF ATLANTIC COD (*Gadus morhua*) FILLETS

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ABSTRACT

This study reports on the protein changes that occur during the storage of frozen cod fillet portions and the relationship of these quality indicators to textural changes in the pressed fish product. Changes in texture and ultrastructure were monitored by determination of moisture, evaporative loss, drip loss, total water loss on cooking and Instron shear force and peak slope measurements on raw and cooked products. Concomitantly, the chemical quality indicators of trimethylamine nitrogen (TMA-N), dimethylamine nitrogen (DMA-N), formaldehyde (HCHO), ammonia (NH_3-N) and free radical content were analyzed to provide information on deteriorative storage changes in the products. Possible alterations in the myofibrillar proteins were determined by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE). High performance liquid chromatography (HPLC) was employed to study the pressure and storage temperature effects on the water soluble sarcoplasmic proteins (SAR). The ultrastructure of the fresh fillets, the pressed triangular and the unpressed fillet block portions were examined by phase contrast light microscopy and scanning electron microscopy. Significant loss ($p \leq 0.05$) in moisture content and increased toughness was seen in the pressed $-12°C$ versus the pressed $-30°C$ cod fillets. This was also reflected in the significantly higher ($p \leq 0.05$) concentrations of DMA-N, HCHO, NH_3-N and free radicals. Results of the SDS-PAGE on the myofibrillar protein extracts showed the disappearance of the ca. 78,500

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daltons protein in the fresh fish. Coincident with the decrease in the concentration of the ➤200,000 daltons proteins in the frozen products, new proteins were observed at ca. 112,000 daltons. An increase in the concentration of the ➤200,000 daltons proteins was also seen upon the addition of 2-mercaptoethanol to the pressed −12°C myofibrillar extract. The HPLC SAR chromatograms showed a 12,000–70,000 daltons profile range. A major decrease was seen in the ca. 23,000 daltons protein for the pressed −12°C extract whereas a major increase was observed in the ca. 34,000 daltons protein for the pressed −30°C extract. Changes at the light and scanning electron microscopy level reflected the storage temperature conditions. Pressure application post rigor to fillets of gadoid fish, such as the cod in this study, did not improve their tenderness, a factor negatively compounded by warm frozen storage conditions.

INTRODUCTION

Little attention has been focused on the relationship between frozen storage and the use of fish for pressurization processing (Love and Karsti 1958). Most investigations have studied the potential tenderization effects of pre- or post rigor pressurization on fresh red meat products (Ivanov *et al.* 1960; Goll *et al.* 1964; Davis *et al.* 1975; Macfarlane *et al.* 1976; Macfarlane and McKenzie 1976; Bouton *et al.* 1977a,b; Macfarlane and Morton 1978; Elgasim and Kennick 1980; Horgan 1981; Elgasim and Kennick 1982; Elgasim *et al.* 1982; Schumann *et al.* 1982; Koohmaraie *et al.* 1983, 1984; Macfarlane *et al.* 1984, 1986; Macfarlane and McKenzie 1986). There appears to be a paucity of information available on the effects of tempering, post rigor pressurization and storage on frozen fish muscle quality and structure. Yet many frozen fish products in today's marketplace have been subjected to the varied processes of freezing, tempering and pressure forming dies. The latter equipment produces fish portions of selected characteristics for either the retail consumer or institutional marketplace. Such portions may be sold plain or subjected to additional processing via breading or battering techniques. The aim of this study was to evaluate the physical, chemical and structural effects of pressure processing on the texture of the post rigor frozen stored cod muscle (*Gadus morhua*) proteins.

MATERIALS AND METHODS

Sample Preparation

Fish samples were obtained as pressed portions and specially prepared unpressed sawn portions from Fishery Products of Newfoundland, Ltd. The por-

tions were prepared from Northern trawl cod which were held on ice for 48h after harvesting. Special care had been taken to ensure that the fish were well bled, gutted and uncrushed during transport to the plant. The fish portions were cut from these high quality cod blocks which were tempered to ca. −5 °C and pressure-formed into triangular wedges or sawn into rectangular portions and individually quick frozen (IQF). These fillet-like portions then were wrapped in polyethylene bags, placed in 2.2 kg waxed cardboard boxes and held in cardboard cases at −30 °C prior to air shipment on dry ice from Newfoundland to Halifax, Nova Scotia. Same day shipments were transported from the airport to the University and aliquoted immediately for storage at −30 °C and −12 °C in microprocessor computer controlled constant temperature compartments for ca. 6 months. Fresh control cod fish were obtained from the live storage tanks of the Fisheries and Oceans Laboratory, Lower Water Street, Halifax, Nova Scotia. The fish were held on ice following decapitation and the control fillets were obtained at 48 h postmortem age (PMA).

Physical Analyses

Moisture. Moisture content was determined in triplicate on ca. 15 g fish samples placed in aluminum foil dishes (Horowitz 1980). The samples were dried to constant weight at 110 °C in a forced air convection oven, cooled in a desiccator and weighed. The loss in weight was reported as percent moisture content.

Water Loss on Cooking. Fillets averaging ca. 1000 g total frozen or fresh wet weight were cooked from the frozen or fresh state on foil covered baking sheets in a standardized 230 °C oven for 24 or 12 min, respectively. The fillets were allowed to cool to room temperature (22 ± 2 °C) and then reweighed to determine the weight change between the raw and cooked product. Data was expressed as a percent of the raw weight.

Instron Texture Evaluation. Objective texture measurements were performed with the Instron Universal Testing Machine Model TM. A Kramer Shear Compression Cell (66 mm × 66 mm) was used at diminished capacity (66 mm × 28 mm, 4 blades) by insertion of two aluminum plates as suggested by Bilinski *et al.* (1977) and modified by Gill *et al.* (1979). The Instron was operated with a cross head speed of 10 cm/min while a recorder speed of 20 cm/min was found convenient. The return gauge was set at 8.35 cm so that the compression cycle terminated just after the blades emerged from the bottom of the test cell. Fillets were tested in both the raw and cooked state. The raw and cooked fillets were cut into ca. 1 cm^3 pieces and 50 g samples were placed into sealed plastic containers. Samples were evaluated with the modified Kramer cell within 30 min of preparation. Peak heights and slopes were tabulated on the basis of sample weight for 10–12 samples of each treatment.

Chemical Analyses

Perchloric Acid Extracts. The frozen fillets were thawed overnight in a refrigerator at 4 °C and were sampled as follows. The thawed and fresh control fish fillets and cut into 1 cm^3 pieces, mixed and 60 g samples were homogenized in 120 mL 6% (w/v) perchloric acid (Ehira *et al.* 1970). Homogenization was accomplished by blending in a precooled Cuisinart, Model RC1 for two one minute intervals and the walls of the food processor jar were scraped down at the end of each interval. The homogenates were filtered through Whatman #1 filter paper and a 100 mL aliquot of the filtrate adjusted to pH 7.0 with a measured quantity of 30% (w/v) KOH. The neutralized extract was refrigerated for 1h to allow $KC10_4$ crystals to precipitate. Suitable aliquots of the extracts were placed into vials, frozen and stored at −30 °C for subsequent analysis.

Trimethylamine. Assays for TMA using the method of Castell *et al.* (1974) were performed in duplicate using the perchloric acid extracts described.

Dimethylamine. Assays for DMA using the method of Castell *et al.* (1974) were performed in duplicate using the perchloric acid extracts described.

Formaldehyde. Assays for HCHO using a modification (Cochin and Axelrod 1959) of the Nash reagent method (1953) were performed in duplicate using the perchloric acid extracts described.

Ammonia. Assays for ammonia were determined by the enzymatic conversion of α-ketoglutarate to glutamate in the presence of ammonia and NADH using the method of LeBlanc and Gill (1984). Analyses were performed in duplicate using the perchloric acid extracts described.

Free Radical Analysis. Trichloroacetic acid (TCA) extracts (Toyomizu *et al.* 1981) also were prepared from the samples. Assays for free radical content (Toyomizu *et al.* 1981) were performed in duplicate on the TCA extracts which had been filtered through Whatman #1 filter paper prior to neutralization. 1,1-diphenyl-2-picrylhydrazyl (DPPH)(Aldrich Chemical Company, Inc.) was used as a free radical. The free radical reactant content of the filtered fish muscle sample extracts was read at 546 nm using a Pye-Unicam SP 800 spectrophotometer. Results were expressed in terms of the decreased amount of DPPH added to the filtered TCA fish muscle extracts.

Preparation of Myofibrils for Electrophoresis. Twenty grams finely divided frozen or fresh control cod muscle was minced in 5 volumes ice cold 100 mM KCl-20 mM KH_2PO_4 (pH 7.0) - 1 mM ETDA - 1 mM NaN_3 using a Lourdes mixer, Model MM1-B and the procedure of Olson *et al.* (1976). The samples were blended at high speed for four 15-s intervals with a 30-s cooling interval between each 15-s run. The medium size stainless steel homogenization container was continually cooled in an ice bath. Homogenates were centrifuged at 600 × g for 15 min at 4 °C. A pellet was formed in two layers consisting of a

highly compacted solid matrix on the bottom and a finely divided upper layer which was carefully removed using a Pasteur pipette. The finely divided sediment was washed and centrifuged six times in cold homogenization buffer as above, while the bottom layer from the first centrifugation was discarded. The myofibrillar material was then washed thrice in ice cold 100 mM NaCl to remove potassium ions. An aliquot was taken for preparation of slides for phase contrast light microscopy. The remaining white myofibrils were then dissolved by suspending a portion of the NaCl washed sediment from the last centrifugation in 2 volumes of either 8 M urea - 2.5% (w/v) SDS - 5 mM EDTA - 100 mM Tris/glycine (pH 8.8) or 8 M urea - 2.5% (w/v) SDS - 5 mM EDTA - 1% (w/v) 2-mercaptoethanol - 100 mM Tris/glycine (pH 8.8). The suspensions were heated in a boiling water bath for 5 min to prevent proteolytic degradation (Weber *et al.* 1972) and dialyzed overnight respectively, against 25 mM Tris/HCl - 0.2% (w/v) SDS (pH 7.4) or 25 mM Tris/HCl - 0.1% (w/v) 2-mercaptoethanol - 0.2% (w/v) SDS (pH 7.4). The reduced, dissociated myofibrillar proteins were then subjected to sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) as described by Porzio and Pearson (1977).

Sodium Dodecyl Sulfate Polyacrylamide Gel Electrophoresis

Electrophoresis was carried out in a Model GE-4 gel electrophoresis apparatus (Pharmacia Fine Chemicals) at 1 mA per tube for 15 min and then at 2 mA per tube for the duration of the run. The molecular weight markers (Sigma Chemical Company) used in preparation of standard curves were as follows: ribonuclease, 13,700; ovalbumin, 45,000; conalbumin, 76,600; bovine serum albumin (BSA) monomer, 68,000; BSA dimer, 136,000; BSA trimer, 204,000; BSA tetramer, 272,000 (Andrews 1970). The BSA polymers were prepared by polymerization of the BSA monomer with glutaraldehyde (Payne 1973). Gels were stained for 1h in Coomassie brilliant blue R-250 (Weber and Osborn 1969) and diffusion destained with 5% methanol - 7.5% acetic acid (v/v). Gels were scanned in a Beckman Model R-112 scanning densitometer.

Preparation of Sarcoplasmic Proteins for High Performance Liquid Chromatography (HPLC). The frozen fillets were thawed overnight in a refrigerator at 4 °C and were sampled as follows. The thawed and fresh control fish fillets were cut into 1 cm^3 pieces, mixed and 50 g samples homogenized in 50 mL cold double distilled deionized water using a Lourdes mixer, Model MM1-B. The samples were blended at high speed for four 15-s intervals with a 30-s cooling interval between each 15-s run. The homogenization container was continually cooled in an ice bath. The homogenates were kept cool on ice and weighed immediately into prechilled centrifuge tubes. The latter were ultracentrifuged at 45,000 × g for 30 min in a Beckman Model L-2 preparative ultracentrifuge with an SW 27 rotor at −5 °C. The supernatant was used immediately for protein profile separation by HPLC.

HPLC of Sarcoplasmic Proteins. The chromatography system consisted of a Waters Associates, Inc. 6000A solvent delivery system operated by a Model 720 System Controller and sample injection by a WISP 710B auto sampler. The eluant was monitored by a Model 450 variable wavelength detector connected to a Data Module 150C. An I-125, I-250 dual protein column system was used (Waters Associates, Inc.) with protein exclusion limits of 80,000 and 500,000 daltons, respectively. The column eluted with 0.07M sodium phosphate buffer, pH 7.0. The flow rate was 2.0 mL/min and the chart speed was 1 cm/min. Ten microliter aliquots of the supernatant were filtered through a 0.22 μM Millipore filter using a 25 mm Swinny filter holder (Millipore Ltd.) prior to HPLC analysis. Samples were then injected and absorption patterns were monitored at 230 nm. Catalase, aldolase, BSA, ovalbumin, α-chymotrypsin and ribonuclease A (Sigma Chemical Company) were used as markers with apparent molecular weights of 210,000; 150,000; 68,000; 45,000; 22,500 and 13,700 daltons, respectively (Andrews 1970). Protein concentration of the supernates was determined by the Lowry *et al.* (1951) method with BSA as a standard.

Microstructural and Ultrastructural Examination

Light Microscopy. Aliquots of the final NaCl myofibrillar washing described in Preparation of Myofibrils for Electrophoresis were used in preparation of slides for phase contrast microscopy. A drop of each myofibrillar suspension was placed on a clean slide, coverslipped and sealed wtih transparent nail varnish. The slides were examined using a Nikon Optiphotomot microscope equipped with phase contrast optics at a magnification of 400x. Myofibrils were photographed using the Microflex HFX photomicrographic attachment and Kodak Technical Pan 2415 film.

Scanning Electron Microscopy. Samples were prepared from each treatment by liquid nitrogen cryofracture followed by immediate fixation with 2.5% glutaraldehyde in 0.2M Sorenson phosphate buffer pH 7.2 for 4h at 4 °C. The samples were washed thrice in buffer at 30 min intervals and then transferred to 1% OsO_4 in 0.2M Sorenson phosphate buffer pH 7.2 for 40 min at 4 °C followed by three rinses in distilled water at 5 min intervals. The fixed samples were dehydrated in a graduated series of acetone-water (v/v) mixtures of 30, 50, 70, 90, 95, 100 and 100%. Each dehydration step took 10 min. The fixed dehydrated samples were dried in a Sorvall Model 49300 critical point drier and gold coated in a Neotech (thin film) S.E.M. Prep 2 sputter coater operated at 200 mTorr, 20 mA and 2-60 s coatings. The specimen stubs were then examined and photographed in a Cambridge Stereoscan scanning electron microscope at 10kV.

Statistical Analyses

Data obtained from the experiment was evaluated using the SAS Statistical Analysis package on the VAX 11/750 at Mount Saint Vincent University.

RESULTS AND DISCUSSION

Physical Analyses

Moisture. The moisture content of the fresh and ca. 6 month frozen stored fish fillet samples (Table 1) was found to be significantly different ($p \leq 0.05$) for each of the treatments. The moisture content ranged between 82.7% for the fresh 48h PMA treatment to 81.5% for the pressed −12 °C treatment. The percent moisture decreased by 0.5% from the fresh fillets to the unpressed fillets stored at −30 °C and by 1% from fresh to both the pressed samples at −12 °C and −30 °C.

TABLE 1.
MOISTURE, EVAPORATIVE LOSS, DRIP LOSS, TOTAL WATER LOSS ON COOKING, PEAK FORCE AND PEAK SLOPE OF FRESH, PRESSED AND UNPRESSED −30 °C AND PRESSED −12 °C COD (*GADUS MORHUA*) FILLETS.

	TREATMENT[1]			
ANALYSIS	Fresh 48h PMA	Pressed -30°C	Unpressed -30°C	Pressed -12°C
H_2O, %[2]	82.69a ±0.04	81.84c ±0.02	82.31b ±0.02	81.51d ±0.02
Evaporative Loss, %[3,5]	11.92a ±0.09	10.40b ±0.04	6.42c ±0.04	10.46b ±0.02
Drip Loss, %[3,5]	10.80a ±0.16	9.92c ±0.04	10.32b ±0.04	10.46ab ±0.06
Total WLC, %[3,5]	22.72a ±0.07	20.32c ±0.09	16.74d ±0.01	20.92b ±0.04
Peak Force, kg/g[4,6]	0.57c ±0.06	1.02b ±0.08	0.64c ±0.07	1.46a ±0.06
Peak Force, kg/g[3,6]	1.20c ±0.08	1.71b ±0.04	1.36c ±0.16	3.20a ±0.19
Peak Slope, kg/cm/g[4,6]	0.23d ±0.02	0.26c ±0.01	0.32b ±0.01	0.69a ±0.02
Peak Slope, kg/cm/g[3,6]	0.57d ±0.06	1.02b ±0.06	0.70c ±0.06	1.58a ±0.10

[1]Values with the same letter are not significantly different ($p \leq 0.05$).
[2]Mean ± s.d. of triplicate analyses.
[3](C) = cooked.
[4](R) = raw.
[5]Mean ± s.d. of duplicate analyses.
[6]Mean ± s.d. of ten analyses.

Moisture losses cannot be explained by a difference in moisture content between the fresh cod caught off Nova Scotia compared with the samples collected and processed into pressed and unpressed frozen portions in Newfoundland. Processing and storage temperature appear to have affected both the pressed and unpressed fillet portions (Table 1). Moisture may have exuded during the tempering and pressurization of the postrigor pressed portions. This postrigor application of pressure to the fish fillet portions may explain why the moisture retention was not higher in the pressurized muscle as had been found by Macfarlane (1973) for prerigor pressurized ox muscle. The postrigor pressure applied to the fish portions appears to have been insufficient to disrupt and expose the hydrophilic groups in the structural proteins. Protein denaturation may have occurred during the freezing process and subsequent storage. This could have contributed to changes in protein quarternary structure viz., filamentous $\rightarrow$ globular, myofibrillar protein fragmentation and protein agglomeration or both through chemical reactions.

Recent frozen storage study data on cod fish fillets held at various storage temperatures for 90 days (LeBlanc, unpublished observations) showed a significant ($p \leq 0.05$) and logarithmic decrease in moisture content. These results support the present data on moisture loss during the frozen storage of the pressed and unpressed cod portions. Such losses could lead to freezer burn, textural changes and overall quality deterioration.

Water Loss on Cooking. Acceptability and consumption of frozen seafood is based in part on the overall flavor and textural quality of the cooked product. Changes in fish fillet texture were measured physically through water loss on cooking (WLC) and Instron Texture evaluation.

Cooking losses were determined by measuring the weight change between the raw and cooked fish muscle and were expressed as a percent of the raw weight. With the preparation method employed, it was possible to separate the total water loss on cooking (WLC) into evaporative loss and drip loss (Table 1). The evaporation or volatile losses were calculated from the difference between the total weight change and the weight of the drippings. The drippings consisted of the material that accumulated in the foil covered baking sheet. These physical indicators of fish quality were much lower in the unpressed $-30\,°C$ fillet treatment. Other researchers (Roberts *et al.* 1974; Davis *et al.* 1975) have also reported a higher percent cooking loss in postrigor pressed rib and tenderloin beef steaks. Conversely, Macfarlane (1973; 1974) and Kennick *et al.* (1980) found reduced cooking losses in prerigor pressurized beef muscle. The difference in total WLC between fresh and pressed $-30\,°C$ fillets was 2.4% while the difference between the fresh and unpressed $-30\,°C$ fillets was 6.0%. The unpressed $-30\,°C$ fillets exhibited ca. 4% lower evaporative loss and total WLC when compared with the pressed $-12\,°C$ treatment.

These results are consistent with the frozen storage study findings on fish reported by other investigators (Reay 1933; Paul and Child 1937; Ramsbottom and Koonz 1939; Hankins and Hiner 1941; Deatherage and Hamm 1960; Law *et al.* 1967; Awad *et al.* 1968, 1969; Winger and Fennema 1976; Miller *et al.* 1980; Lee 1982). Drip loss appears to be increased by warm freezer storage temperatures. The explanation generally offered is that the high ionic strength of the solution in the fish muscle causes rapid denaturation of the proteins at the warmer freezer storage temperatures. Lack of water binding is seen as a consequence. Formation of larger ice crystals at the warmer freezer storage temperatures can also contribute to rupture of the muscle structure and concomitant loss of fluid. The lower content of stroma proteins in fish as compared to red meat may make fish muscle more fragile. This effect is not observed at colder freezer storage temperatures because of reduced reaction rates and formation of smaller ice crystals (Love 1958; Giddings and Hill 1978). Juiciness of the fish muscle would also be reduced due to this loss in water holding capacity as evidenced by the evaporative, drip and total WLC data. Such WLC during storage under the various treatment conditions appears characteristic of what would be expected if progressive crosslinking of the myofibrillar proteins was occurring.

The increase in WLC due to pressure was greater when the treatment was held at a warm frozen storage temperature. Such results are likely due to a combination of factors viz., membrane damage, protein fragmentation, protein structural changes, accelerated protein agglomeration due to pressure, temperature, ice crystal formation, changes in ionic strength and low temperature enzyme activity or both. The higher WLC values for the fresh fillets compared with the various frozen fillet treatments may be due to the amount of 'capillary' and 'free' moisture available for evaporation during cooking. Statistical analysis showed no significant correlation between moisture loss and WLC or its partitioned factors of evaporative loss and drip loss (Table 3).

Instron Texture Evaluation. Peak force and peak slope (Fig. 1) are indicators of texture quality which change with environmental conditions (Gill *et al.* 1979) such as temperature and pressure (Table 1). The order of decreasing peak force and slope was pressed $-12\,°C$ > pressed $-30\,°C$ > unpressed $-30\,°C$ > fresh 48h PMA with similar changes seen for both raw and cooked samples. The Instron measurements of peak force and peak slope on the raw and cooked samples were indicative of sample toughening. This finding is in contrast to similar analyses conducted on red meat (Macfarlane 1973; Bouton *et al.* 1977b; Kennick *et al.* 1980; Elgasim and Kennick 1982) where a substantial tenderizing effect was evident. Postrigor fish muscle pressurization combined with the adverse effects of the trimethylamine oxidase enzyme system common to gadoid species may have counteracted any potential tenderization effects on

the myofibrillar structure. Uncontracted postrigor fish muscle would not be subjected to myosin filaments being forced into Z discs.

The Instron force deformation curves (Fig. 1) showed the pressed −12 °C fillet portions to be significantly ($p \leq 0.05$) tougher (Table 1), having both a higher peak force and a steeper slope in the region of compression without shear. Significant changes ($p \leq 0.05$) were also evident in the pressed −30 °C fish fillet

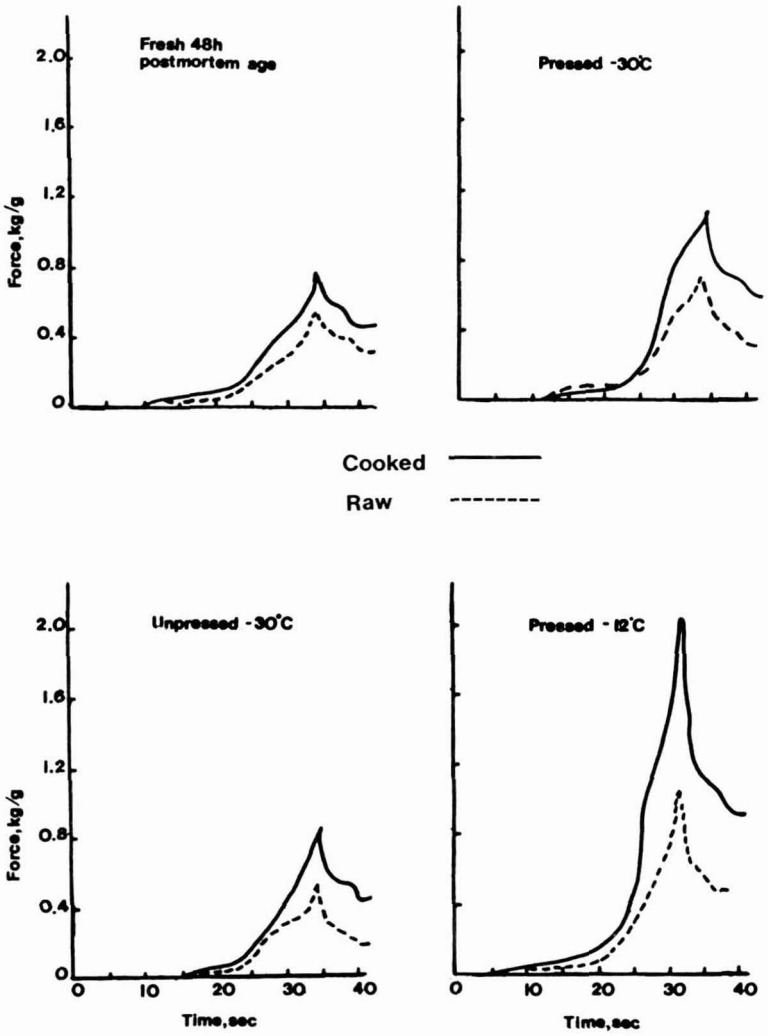


FIG. 1. REPRESENTATIVE EXAMPLES OF INSTRON TEXTURE PROFILES FOR FRESH, PRESSED AND UNPRESSED −30 °C AND PRESSED −12 °C RAW AND COOKED COD (*GADUS MORHUA*) FILLETS

portions in comparison with the fresh and unpressed −30 °C treatments. With the exception of the pressed −30 °C fish fillet portions, the cooked peak force and slope were 200% higher when compared with similar raw products. A significant negative ($p \leq 0.05$) correlation was observed between the fillet moisture content and the Instron texture measurements of peak force and peak slope for raw and cooked samples (Table 3). No significant correlation was observed between WLC and any of the raw or cooked peak force or peak slope texture parameters. Polymerization of fish protein fractions has been attributed to cause the increased peak force and slope evident during frozen storage of fish fillets (Gill *et al.* 1979).

Chemical Analyses

TMA-N, DMA-N, HCHO, NH_3-N and Free Radical Content. The results for each of these parameters for the four treatments is presented in Table 2. With the exception of the fresh 48h PMA treatment where in no TMA-N was detected, there were no significant differences ($p \leq 0.05$) among the treatments for this chemical indice. Temperature change effects were more pronounced for the pressed −30 °C treatment in comparison with the corresponding unpressed fillets when DMA-N, HCHO, NH_3-N and free radical content were analyzed as indicators of frozen storage quality deterioration. With the exception of TMA-N, the ratio of all the parameters for the pressed to unpressed fillets stored at −30 °C was > 1. DMA-N, HCHO and NH_3-N content were significantly different ($p \leq 0.05$) for the pressed −12 °C and −30 °C treatments. A ratio > 1 was also found between these two treatments. Table 2 shows that the pressed fillets at −12 °C were ca. six times higher in DMA-N and ca. 3.8 times higher in HCHO than the treatments at −30 °C. An equimolar DMA:HCHO ratio was not found. This was probably due to the binding of the HCHO to the protein. The NH_3-N and free radical content exhibited a similar trend. There were significant differences ($p \leq 0.05$) among all treatments for the NH_3-N and free radical content. The appearance of all these compounds except TMA-N in the fresh 48h PMA cod fillets may be indicative of natural background levels or freezing upon ice contact.

Significant negative correlations ($p \leq 0.05$) were found between moisture loss and the quality indicators of DMA-N, HCHO, NH_3-N and free radical content (Table 3). These quality indicators showed a significant positive correlation between each other and with the texture indicators of peak slope and force for both raw and cooked products.

SDS-PAGE of the Myofibrillar Proteins. Increased textural deterioration in fish can be monitored by both increased Instron shear force and peak slope or by changes in the myofibrillar proteins (Gill *et al.* 1979). These protein changes are reflected by molecular weight changes due to covalent bonding which can be

TABLE 2.
TMA-N, DMA-N, HCHO, NH_3-N AND FREE RADICAL CONTENT OF FRESH, PRESSED AND UNPRESSED −30 °C AND PRESSED −12 °C COD (*GADUS MORHUA*) FILLETS.

	TREATMENT[1]			
ANALYSIS	Fresh 48h PMA	Pressed -30°C	Unpressed -30°C	Pressed -12°C
TMA-N, mg%[2]	0.00b ±0.00	0.44a ±0.01	0.57a ±0.06	0.39a ±0.07
DMA-N, mg%[2]	0.10c ±0.01	0.80b ±0.02	0.77b ±0.01	4.82a ±0.04
HCHO, umoles%	4.02c ±0.04	8.66b ±0.05	6.21c ±0.22	28.22a ±1.11
NH_3-N, mg%[2]	3.64d ±0.02	12.50b ±0.01	9.65c ±0.01	15.28a ±0.01
Free Radicals, umoles/g[2]	102.51d ±0.01	813.46b ±0.01	687.99c ±0.01	1231.66a ±0.01

[1]Values with the same letter are not significantly different ($p \leq 0.05$).
[2]Mean ± s.d. of duplicate analyses.

monitored by SDS-PAGE. The results of the SDS-PAGE on the myofibrillar proteins of the fish muscle from the four treatments tested are presented in Fig. 2. From inspection of the densitometric scans and calculation of the percent area of the major peaks, changes in the proteins can be seen. The major change in the SDS-PAGE densitometric scans of the fresh and frozen fish fillets is the disappearance of a protein at 78,500 daltons and the concomitant appearance of a protein at 112,000 daltons in the frozen fillet samples. Other changes include the disappearance of the proteins at ➤200,000 daltons in the unpressed −30 °C and the pressed −12 °C fillets. Their disappearance during storage in the unpressed −30 °C and the pressed −12 °C fillets may be due to protein agglomeration through either covalent S-S bonds or formaldehyde induced crosslinks. The presence of the very high molecular weight proteins in the pressed −30 °C fillets could be due to alterations in myosin following the tempering and pressurization treatments. Work by Ivanov *et al.* (1960) found that the molecular weight of myosin in solution increased when subjected to pressure.

Figure 3 presents the same myofibrillar protein extracts subjected to SDS-PAGE as previously discussed but with the addition of a reducing agent, 2-mercaptoethanol. Little or no change was observed in the densitometric scans of either the fresh 48h PMA or pressed −30 °C myofibrillar proteins fractions treated with 2-mercaptoethanol. These observations show that the fresh 48h

TABLE 3.
CORRELATION MATRIX FOR CHEMICAL AND PHYSICAL ANALYSES OF FRESH, PRESSED AND UNPRESSED −30 °C AND PRESSED −12 °C (*GADUS MORHUA*) FILLETS.[1,2]

	TREAT-MENT	H_2O	TMA-N	DMA-N	HCHO	NH_3-N	FREE RADICALS	EVAP. LOSS	DRIP LOSS	TOTAL WLC	INPFR	INPFC	INPSR	INPSC
TREAT-MENT	1.000	-0.200	-0.916***	-0.120	-0.150	0.396	0.370	-0.906***	-0.686	-0.954***	-0.068	-0.144	-0.106	-0.052
H_2O		1.000	-0.543	-0.816**	-0.840**	-0.978****	-0.962****	0.004	0.539	0.084	-0.926****	-0.882****	-0.774**	-0.960****
TMA-N			1.000	0.245	0.218	0.698*	0.685	-0.794*	-0.736*	-0.857**	0.190	0.299	0.201	0.351
DMA-N				1.000	0.996****	0.770*	0.838**	0.085	0.013	0.082	0.934***	0.991****	0.994****	0.901**
HCHO					1.000	0.782*	0.840**	0.146	-0.018	0.134	0.957***	0.996****	0.984****	0.925***
NH_3-N						1.000	0.988****	-0.206	-0.612	-0.284	0.818**	0.834**	0.712*	0.903**
FREE RADICALS							1.000	-0.242	-0.504	-0.303	0.840**	0.884**	0.792**	0.906**
EVAP. LOSS								1.000	0.326	0.990****	0.262	0.084	0.079	0.177
DRIP LOSS									1.000	0.456	-0.141	-0.102	0.106	-0.348
TOTAL WLC										1.000	0.226	0.064	0.090	0.115
INPFR											1.000	0.940****	0.856****	0.970****
INPFC												1.000	0.954****	0.965****
INPSR													1.000	0.893****
INPSC														1.000

[1]Table 1 details the abbreviated headings used.
[2]* Significant at $p \leq 0.05$.
[2]** Significant at $p \leq 0.01$.
[2]*** Significant at $p \leq 0.001$.
[2]**** Significant at $p \leq 0.0001$.

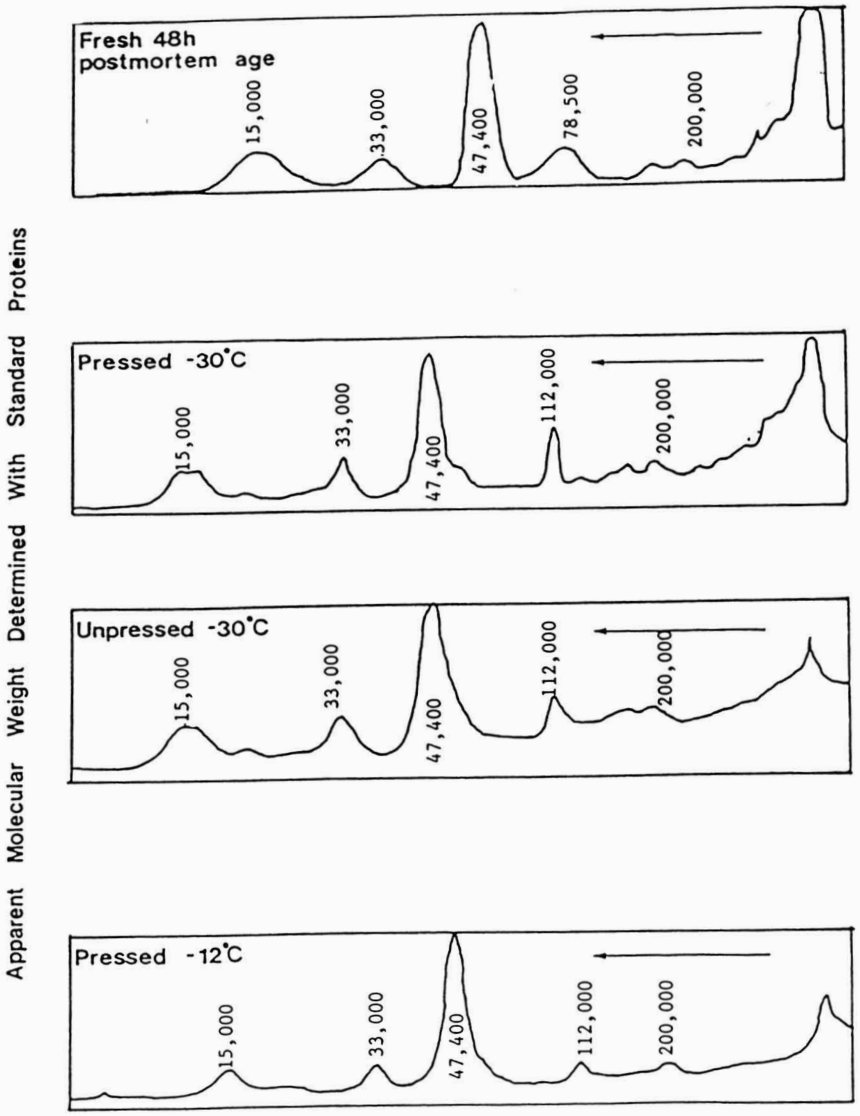


FIG. 2. DENSITOMETRIC SCANS OF SDS-PAGE GELS OF FRESH, PRESSED AND UNPRESSED −30 °C AND PRESSED −12 °C COD (*GADUS MORHUA*) MYOFIBRILS

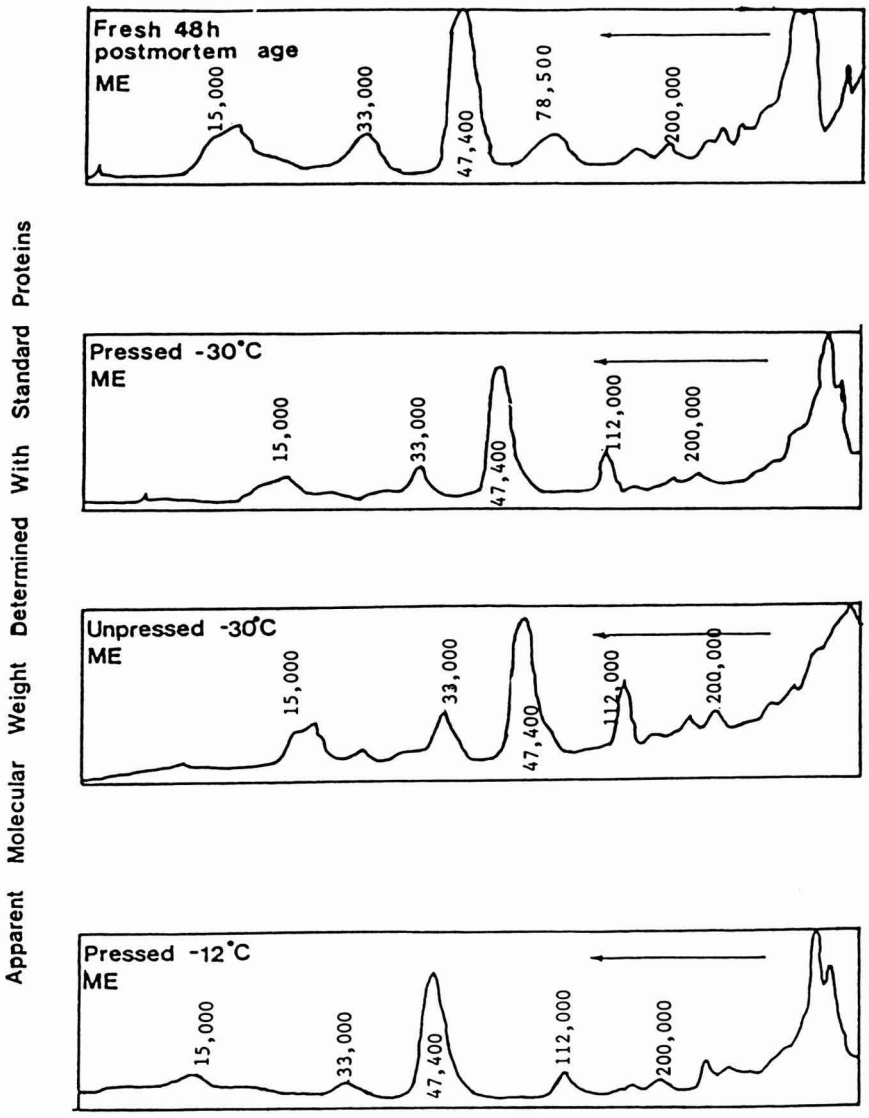


FIG. 3. DENSITOMETRIC SCANS OF SDS-PAGE GELS OF FRESH, PRESSED AND UNPRESSED −30 °C AND PRESSED −12 °C COD (*GADUS MORHUA*) MYOFIBRILS TREATED WITH MERCAPTOETHANOL (ME)

PMA fillets did not contain covalent S-S bonds nor did the addition of 2-mercaptoethanol promote their occurrence. The pressed −30 °C myofibrillar protein fractions appear to contain fragmented or covalently bonded polymerized proteins which could not be broken by the reducing agent used. Conversely,high molecular weight proteins increased in the pressed −12 °C myofibrillar proteins treated with 2-mercaptoethanol. This may have resulted from a breakdown of covalent S-S crosslinks produced because of the warmer frozen storage conditions.

HPLC of the Sarcoplasmic Proteins. Low molecular weight proteins soluble in water were separated from water insoluble proteins by ultracentrifugation. Their solubility at very low ionic strength allowed them to be classified as sarcoplasmic proteins (SAR). Little information appears available on the composition of the SAR as related to the effects of processing, temperature and frozen storage conditions.

The HPLC profile of the water soluble proteins for the four treatments evaluated is shown in Fig. 4. Visual inspection confirms the need either to increase the number of column plates or to use additional chromatographic parameters to obtain a higher separation number between some of the peaks. This is particularly needed for those peaks at 50,000, 22,000 and 12,000 daltons, respectively. Such increased separation of the water soluble proteins could provide more detailed information on the effects of pressure and temperature.

Nevertheless, from the electronically determined area under the HPLC peaks, changes were evident in the SAR analyzed by the HPLC column under the stated chromatographic conditions. The area ratio of the peaks corresponding to proteins of molecular weights of 23,000 and 20,000 daltons, respectively, were lower in the pressed −12 °C cod fillets than in the other three treatments. The apparent decrease in the peak at ca. 23,000 daltons could be indicative of either protein hydrolysis or polymerization to higher molecular weight proteins. The respective ratio between the peaks at 34,000 and 23,000 and 34,000 and 20,000 daltons also shows differences among the various treatments. The pressed frozen fillets stored at −30 °C were higher for this peak ratio than were the other samples. The pressed −12 °C fish fillets showed the appearance of new proteins being formed at molecular weights between 34,000 and 23,000 daltons, respectively. Even though negligible in quantity, these peaks may reflect increased covalent bonding of lower molecular weight proteins during frozen storage. This may have been incurred through increased production of formaldehyde, S-S bonding or a composite effect of these in conjunction with the pressure and frozen storage conditions. The SAR of the fresh fish fillets showed a slightly higher total area percent for the peaks at 23,000 and 20,000 daltons, respectively. The percent of these two peaks remained constant for the frozen storage treatments. Figure 4 also shows that the profile at >50,000 daltons for pressed

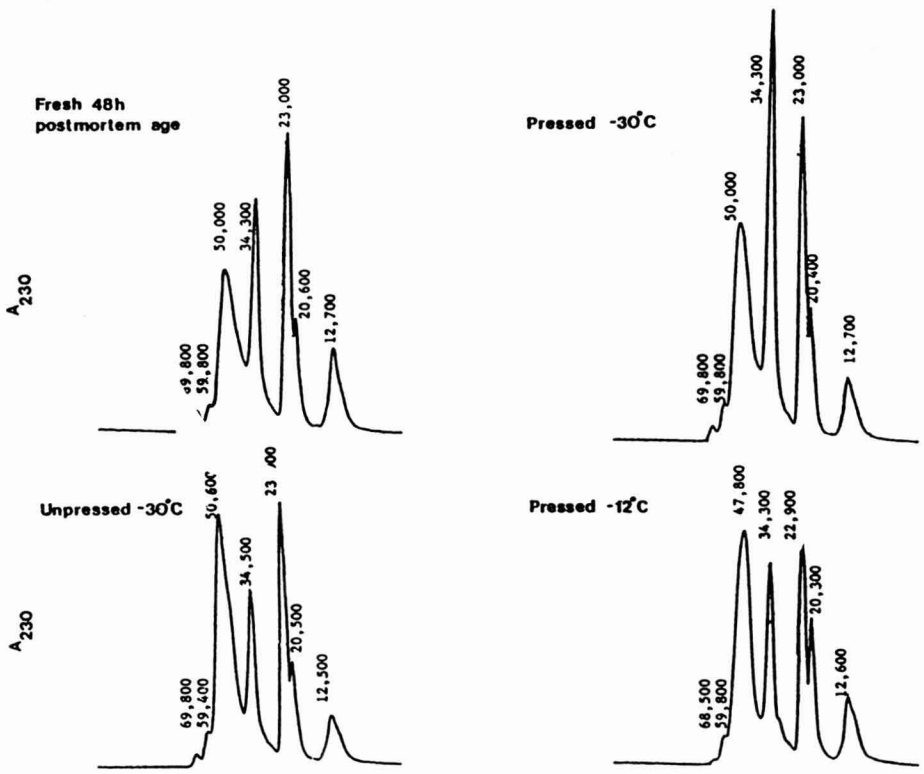
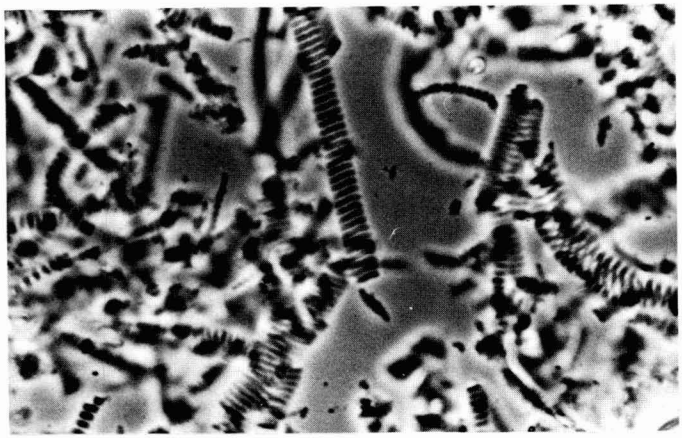


FIG. 4. HPLC PROFILES OF THE SARCOPLASMIC PROTEINS OF FRESH, PRESSED AND UNPRESSED −30 °C AND PRESSED −12C COD (*GADUS MORHUA*) FILLETS

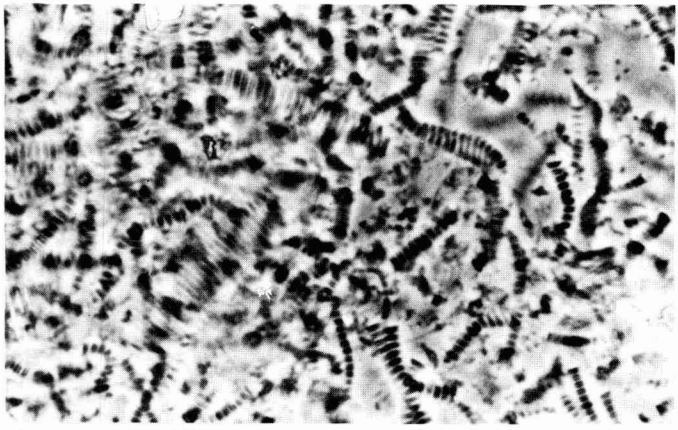
−12 °C fillets differed substantially from that for the fresh 48h PMA fillets. The 69,800 daltons protein apparent in the fresh 48h PMA fillets is not evident in the pressed −12 °C fillet treatment. Minor but potentially significant changes for SAR of rabbit *Longissimus dorsi* muscle were also noted by Horgan (1979) for molecular ranges similar to those in the present investigation.

Microstructure and Ultrastructural Examination

Light Microscopy. A Nikon Optiphotomot microscope equipped with phase contrast optics was used to examine myofibrillar extracts from the various sample treatments. The results, recorded using Kodak Technical Pan 2415 film, are presented in Fig. 5. Intact myofibrils were evident in the fresh 48h PMA myofibrillar extract. Some fragmentation was evident in the pressed −30 °C myofibrillar extracts whereas less fragmentation was seen in the extracts of the unpressed −30 °C treatment. The pressure and temperature treatments appear to

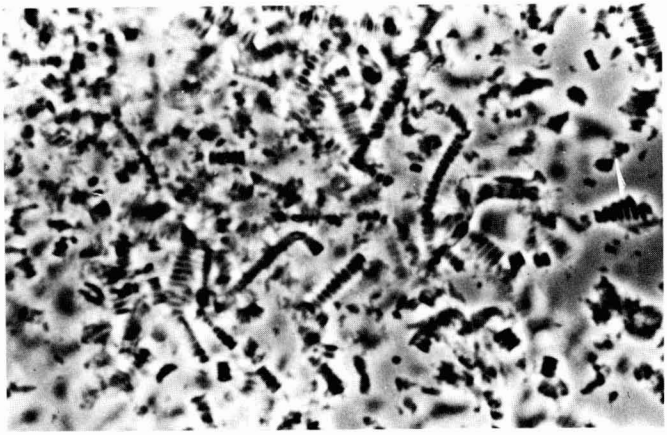


Fresh 48h postmortem age



Unpressed -30°c

FIG. 5. PHASE CONTRAST LIGHT MICROGRAPHS OF COD (*GADUS MORHUA*) MYOFIBRILLAR EXTRACTS (× 2000) Fresh and unpressed −30 °C



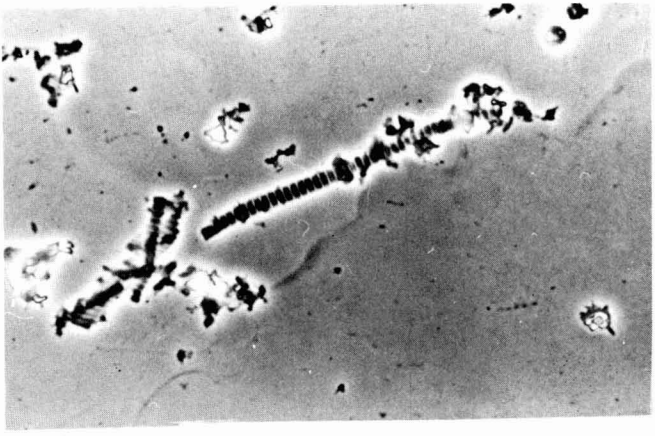


FIG. 5. PHASE CONTRAST LIGHT MICROGRAPHS OF COD (*GADUS MORHUA*) MYOFIBRILLAR EXTRACTS (× 2000) Pressed −30 °C and Pressed −12 °C

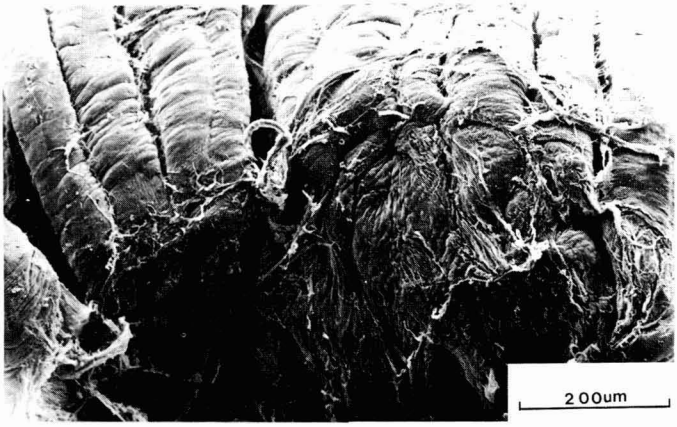


FIG. 6. SCANNING ELECTRON MICROGRAPHS OF COD (*GADUS MORHUA*) FILLETS
Fresh and Unpressed −30 °C

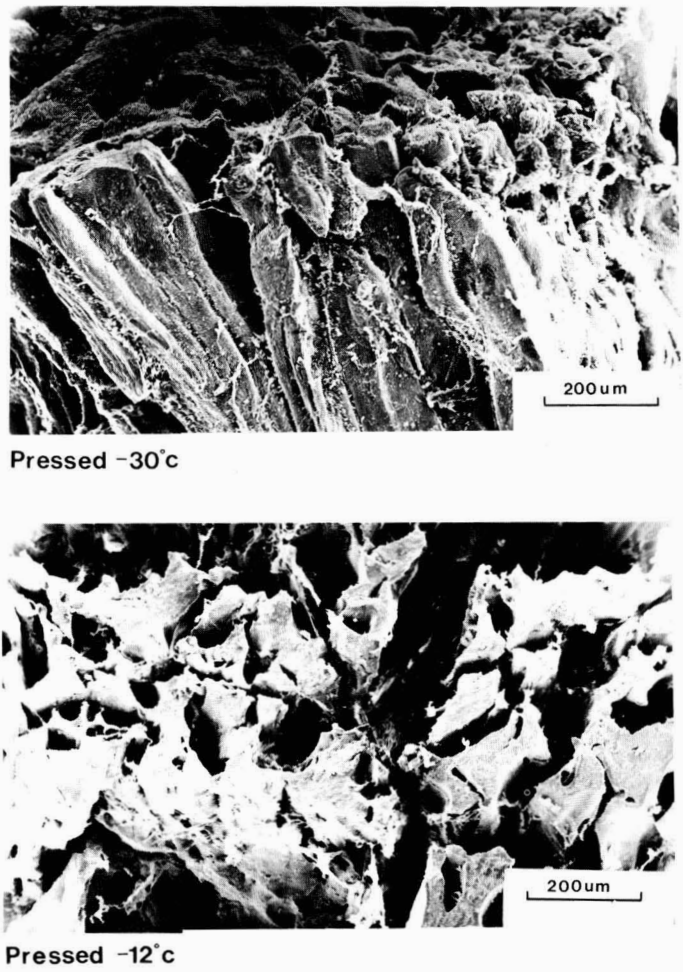


FIG. 6. SCANNING ELECTRON MICROGRAPHS OF COD (*GADUS MORHUA*) FILLETS
Pressed −30 °C and Pressed −12 °C

have resulted in severe disruption of the myofibrillar structure. This is very evident in the myofibrillar extracts of the pressed −12 °C treatment. Much smaller fiber pieces, a higher degree of fragmentation and a lower degree of protein extractability were observed. The latter supports the temperature sensitivity of fish proteins to storage conditions which promote insolubilization of the myofibrillar proteins (Dyer 1951; Love 1983; Lim and Haard 1984).

Scanning Electron Microscopy. Samples from all treatments were prepared by cryofracture and appropriate fixation for examination by SEM. Photographic results are presented in Fig. 6. There appeared to be a higher level of distortion and sponginess in the appearance of the pressed −12 °C fish fillets. Damage is more severe due to the large extracellular ice crystals causing tissue dehydration, shrinkage and compaction. There is virtually no space between the myofibrils and the sarcoplasmic reticulum seems compressed into a thin layer. The reduction in sarcoplasmic space and the compression of the sarcoplasmic reticulum appears greater at the warmer frozen storage temperature. Less alteration was evident in the muscle structure of the unpressed −30 °C treatment than was apparent in the pressed −30 °C fish fillets. Structural damage was probably less pronounced due to the formation of tiny intracellular ice crystals which caused minimum dislocation of tissue ultrastructural components. The appearance of postrigor pressurized cod fillets was very different from that of prerigor pressurized red meat (Bouton *et al.* 1977b; Kennick *et al.* 1980; Elgasim and Kennick 1982; Riffero and Holmes 1983). It appears from the present observations that pressurization postrigor does not disrupt the sarcolemma and reduce the connective tissue associated with the endomysium. Observation of the raw postrigor pressure treated fish muscle did not reveal extensive fiber fraying (Fig. 6). Other researchers (Kennick *et al.* 1980; Riffero and Holmes 1983) have reported that contraction caused during the prerigor pressure treatment of beef semitendinosus muscle resulted in pronounced fiber fraying and disruption of the sarcolemma. It appears from examination of the SEM micrographs in Fig. 6 that such contraction did not occur in the postrigor pressurization treatments. Temperature effects seem to be the major cause of the myofibrillar distortion observed.

SUMMARY AND CONCLUSIONS

In this study, the physical, chemical and ultrastructural changes in frozen Atlantic cod fillets muscle were investigated as a function of pressure, temperature and storage. Pressure and warm storage temperature significantly increased muscle toughness in the fish portions as monitored by corresponding increases in the chemical indicators of frozen storage quality. Pressure and/or

temperature contributed to significant changes in the protein profile of both the myofibrillar and sarcoplasmic fractions. Structural changes observed using light and SEM showed greater myofibrillar fragmentation and increased intercellular ice crystal formation which facilitated tissue compaction in the cod portions stored at the warm temperatures.

The results of this study indicate that the best product frozen storage conditions were at temperatures much lower than −12 °C. Tempering and postrigor pressurization of gadoid cod fish muscle did not result in increased tenderness, a factor compounded negatively by warm frozen storage temperatures. As with red meat, it appears that any practical application of pressurization must lie in its use prerigor. This does not seem highly feasible when fish harvesting is considered. Further research should be implemented by producers of convenience retail and institutional fish portions from restructured comminuted muscle tissue to investigate pressurization for binding in combination with permitted cryoprotectants to prevent major textural deterioration from producer to consumer.

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DEVELOPMENT AND EVALUATION OF A PROCEDURE TO PRODUCE MESQUITE (*Prosopis* spp) POD PROTEIN CONCENTRATE[1]

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ABSTRACT

*Four variations of a mechanical process for producing a mesquite (*Prosopis *spp.) pod protein concentrate were studied. All involved pin milling and dry sieving and one included toasting prior to grinding. Dry sieving concentrated the protein in the fine (−100 mesh) fraction. The process utilizing toasting gave maximum protein recovery and low fiber concentration in the fines. In vitro digestibilities of the coarse (+45 mesh) and intermediate (+100 mesh) fractions indicated their suitability for ruminant feeds.*

INTRODUCTION

Mesquite (*Prosopis* spp.) is a leguminous plant which grows wild in many developing countries (Allen and Allen 1981). It bears pods which contain approximately 13% protein, 21% sugars (mostly sucrose) and 19% crude fiber (Becker and Grosjean 1980; Del Valle *et al.* 1983). Pod protein, possessing a corrected Protein Efficiency Ratio (PER) of 1.4 (Del Valle *et al.* 1983), has been

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found to be limiting in threonine and sulfur amino acids, and borderline in lysine (Becker 1984; De Lumen *et al.* 1985) with respect to the FAO/WHO (1973) pattern for children. Variations in seed protein and amino acid content have been reported by De Lumen *et al.* (1985). Mesquite pods have been found to be almost totally devoid of trypsin inhibitor (1.4 TIU/mg; Del Valle *et al.* 1983) and cyanogenic compounds (Becker and Grosjean 1980). Mesquite pods, therefore, represent a good low-cost protein and calorie source for inhabitants of developing countries. Pod utilization could be enhanced, however, if some means for concentrating protein and decreasing the high fiber content could be found.

In previous work, Del Valle *et al.* (1986) studied a number of processes aimed at obtaining a mesquite pod protein concentrate. In all of these processes, either raw pods or pods which had been subjected to different pretreatments (extrusion and/or toasting) were ground 1 or 4 times in an Alpine pin mill, and the resulting material was separated into +45, +100 and −100 mesh fractions. It was found that in all cases, protein was concentrated and fiber reduced in the fines (−100 mesh fraction), with respect to the original pods.

Of the different pretreatments studied, extrusion, either of whole pods or of pods in a 50/50 blend with soybeans, resulted in maximum protein recovery and concentration in the fines. Considerable difficulty, however, was experienced in extruding the pods without plugging the extruder. Although addition of soybeans to mesquite pods eliminated the extrusion difficulty, the resulting protein concentrate was no longer 100% mesquite. Finally, the need to grind materials 4 times in the mill was considered to be undesirable, since this would raise processing costs.

The purpose of this work, therefore, was to evaluate an alternative mechanical process, which does not utilize extrusion, for producing the protein concentrate.

MATERIALS AND METHODS

Four experimental variations of a mechanical process for obtaining a mesquite pod protein concentrate were evaluated. The variations, summarized in Fig. 1 through 4, were as follows.

Process 1 (Fig. 1).

Raw mesquite pods were passed one time through the Alpine pin mill (Model A400CW, Alpine American Corporation, Natick, MA 01760) with only the door disc rotating in order to break up the pods. The resulting material was then ground four times in the same mill with both discs rotating. The ground material was screened in a U.S. Std. 100-mesh sieve. Yields, proximate chemical

analyses (moisture, ash, ether extract and crude protein, AOAC, 1970) and acid detergent fiber and its components (cellulose, lignin and silica; Goering and Van Soest 1975) of both intermediate (+100 mesh) and fines (−100 mesh) were determined. Yields were based on weights of screened material. Protein recoveries in all materials were calculated by carrying out material balances, based on results of sieve and proximate analyses.

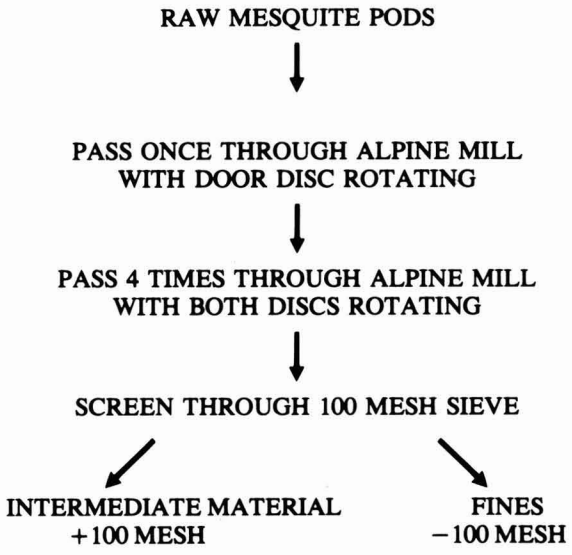

FIG. 1. FLOW DIAGRAM FOR PROCESS 1

Process 2 (Fig. 2).

Raw mesquite pods were passed one time through the Alpine mill with the door disc rotating, after which they were ground one time in the same mill with both discs rotating, rather than the 4 times used in Process 1. The ground material was screened in a U.S. Std. 45 mesh sieve. The resulting coarse material (+45 mesh) was saved and the material which passed through the 45 mesh screen further screened in a U.S. Std. 100 mesh sieve. The products resulting from both screenings were identified as follows: +45 mesh, "coarse material", +100 mesh, "intermediate fraction"; −100 mesh, "fines." As before, yields, proximate chemical analysis, acid detergent fiber and its components, and protein recoveries in all three fractions were determined. The purpose of this experimental variation was to evaluate the effects of additional milling on in vitro digestibility and yields.

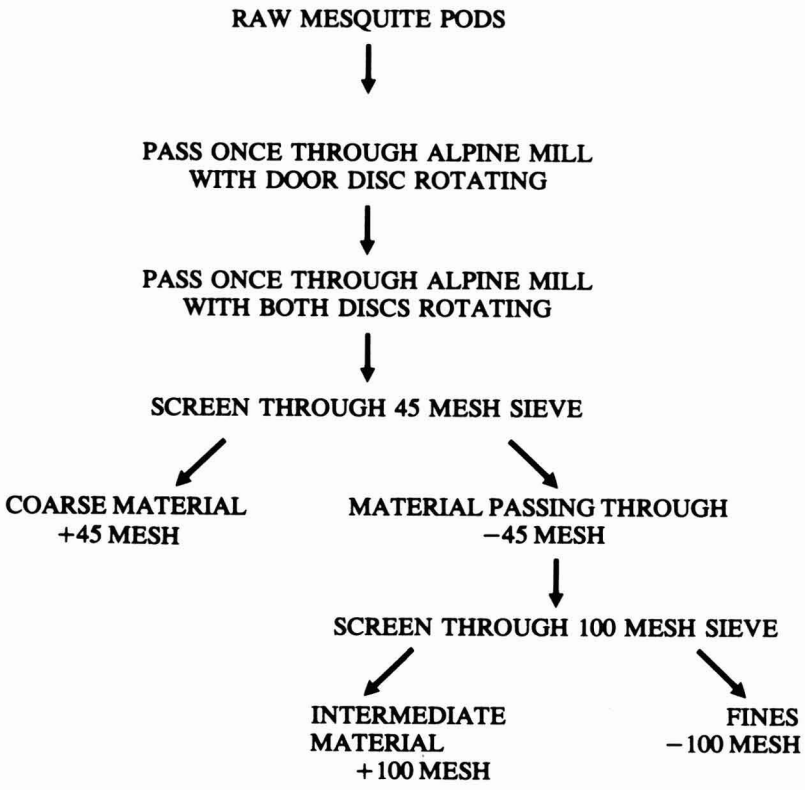

FIG. 2. FLOW DIAGRAM FOR PROCESS 2

Process 3 (Fig. 3).

Raw mesquite pods were fed directly to the Alpine mill with both discs rotating, after which the ground material was screened and processed as described for Process 2. This experiment was designed to demonstrate if the preliminary grinding step, utilizing the Alpine mill with the door disc rotating as in Process 2, was necessary or could be omitted.

Process 4 (Fig. 4).

Raw mesquite pods were toasted (155 °C, 20 min) utilizing a toaster as described by Del Valle *et al.* (1986). The toasted product was ground one time in the Alpine pin mill with both discs rotating, after which the ground material was screened through 45 and 100 mesh sieves as described for Process 2. This experiment was to determine if toasting would improve protein concentration and recovery with respect to yields obtained in the first three processes.

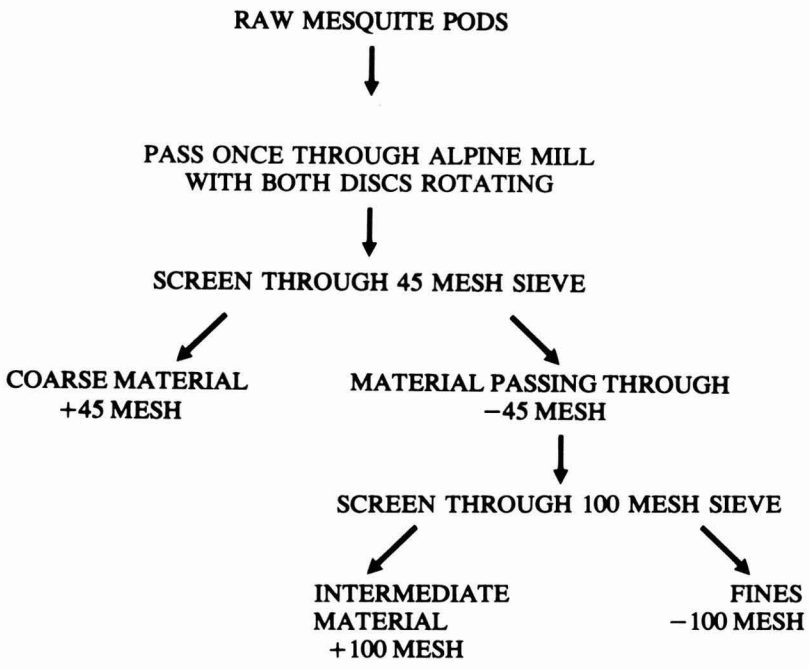

FIG. 3. FLOW DIAGRAM FOR PROCESS 3

The coarse and intermediate fractions (+45 mesh and +100 mesh, respectively) obtained from mesquite pods in all of the above processes were evaluated for ruminant feeding by in vitro digestibility determinations according to the method of Tilley and Terry (1963).

For purposes of comparison, proximate chemical analyses (AOAC 1970) and acid detergent fiber and its components (Goering and Van Soest 1975) of whole raw pods were determined.

RESULTS AND DISCUSSION

Table 1 reports yields of the fractions (+45, +100, −100 mesh) obtained by the four experimental variations of the mechanical process. As expected, Process 1, with four passes through the mill, gave the maximum yield of fines (75.4%). Since in this case the yield of +45 coarse material was so small, it was combined with the +100 mesh intermediate material (data not shown). The primary effect of milling four times (Process 1) was an increased fiber content of

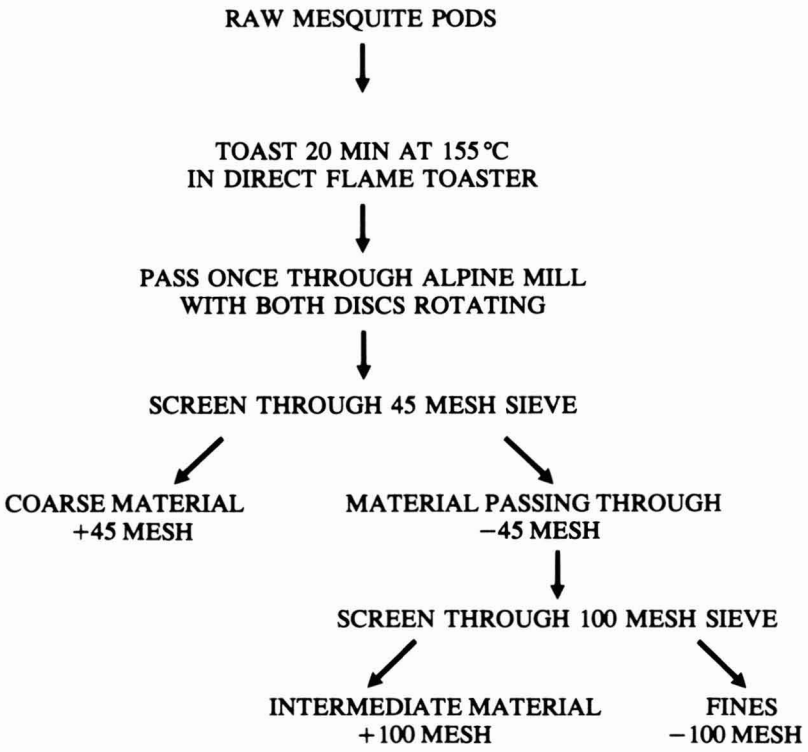

FIG. 4. FLOW DIAGRAM FOR PROCESS 4

the fine material, as shown by elevated ADF, cellulose, and lignin values (Table 1). Yields of fines in Process 2 and 3 were substantially lower than in Process 1 and approximately equal, which demonstrated that the preliminary pass through the Alpine mill with one disc rotating was ineffective in increasing yields.

The effect of toasting on milling characteristics can be seen by comparing the yield of fines from Process 4 with yields obtained in other processes, especially Process 1. Toasted pods required only one pass through the mill to produce over 1/3 more fine material than from similarly treated raw pods (Processes 2 and 3). Toasting (Process 4) yields of fine material nearly equaled the yields obtained in Process 1, in which raw pods were extensively milled by four passes through the mill (69.1% vs. 75.4%).

The results of proximate chemical analyses of the starting material and the fractions from the four different processes are also shown in Table 1. Protein contents of the fines ranged from 12.50–14.40%, depending on the process used. These values are greater than for whole pods, which contained only 11.2% protein. In all cases, protein content increased with increasing mesh number (finer material).

TABLE 1.
YIELD AND PROXIMATE CHEMICAL ANALYSIS OF RAW AND FRACTIONATED MESQUITE PODS

Process	Sieve Mesh	Yield %	Moisture %	Protein[a] %	Fat[b] %	Ash %	ADF[c] %	Cellulose %	Lignin %
Raw Material	---	100	4.90	11.20	1.68	4.60	28.61	20.13	9.05
I	+45	N.A.	N.A.[d]	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	+100	24.6	3.60	11.30	1.83	3.58	47.17	37.97	11.75
	-100	75.4	4.06	12.50	3.45	4.64	26.61	16.79	5.11
II	+45	37.6	3.72	6.00	1.42	4.11	59.74	48.34	13.29
	+100	20.8	3.60	6.90	1.65	3.02	43.73	33.31	11.56
	-100	41.6	3.62	14.40	4.45	4.52	16.69	13.34	4.79
III	+45	40.5	3.42	8.50	1.98	4.82	37.38	30.27	10.40
	+100	16.9	4.31	9.43	2.16	3.72	35.06	27.54	7.19
	+100	42.6	3.23	13.99	5.50	5.06	14.24	10.44	4.33
IV	+45	22.0	2.70	3.65	1.44	4.05	64.46	52.42	13.31
	+100	8.9	3.33	5.89	1.55	2.64	46.31	38.11	12.13
	-100	69.1	3.06	14.33	2.37	4.89	16.25	10.77	4.16

a. Protein = N × 6.25
b. Fat = ether extract
c. ADF = acid detergent fiber
d. N.A. = Not Available

Ether extractable material also increased with increasing mesh number, although this variation was small. Ash tended to decrease and subsequently increase with increasing mesh number, with lowest ash content in the +100 mesh samples. Values for acid detergent fiber and its components decreased with increasing mesh number in all cases. Generally, fiber content of the fines from processes 2–4 were approximately one-half that of whole pods (approximately 14–17% vs approximately 29%). Fines from Process 1 contained approximately the same amount of ADF as whole pods. Silica was not found in any fraction (data not shown).

Table 2 reports protein recoveries in the fines. Maximum recovery was from Process 4, while minimum protein recovery resulted from Processes 3 and 2. These values reveal that, under similar conditions, grinding in the Alpine mill four times with both discs rotating resulted in considerably greater protein recovery than grinding one time; also, pregrinding in the mill with the door disc rotating produced a small increase in protein recovery. The most interesting observation, however, is that toasting the pods before grinding once with both discs rotating resulted in a higher protein recovery (88%) in the fine fraction than grinding raw pods four times (77% recovery).

TABLE 2.
DISTRIBUTION OF TOTAL PROTEIN AMONG THE FRACTIONS FOR THE DIFFERENT PROCESSES

Process	Percent of Total Protein		
	+45 Mesh	+100 Mesh	-100 Mesh
1	--	22.8	77.2
2	23.3	14.9	61.8
3	31.3	14.5	54.2
4	7.1	4.7	88.2

Of the four process variations studied in this work the optimum one appears to be Process 4 for the following reasons: (1) only one pass through the mill with both discs rotating was required; (2) pregrinding in the Alpine mill with the door disc rotating was not required; (3) yield of fines was high, and nearly equaled that obtained with raw pods passed four times through the mill; (4) protein was concentrated and fiber reduced in the fines with respect to raw pods; (5) protein recovery in the fines was the highest obtained in this study; and (6) the process is simple and inexpensive.

Table 3 presents results of the in vitro digestibility determinations. Digestibilities were within the acceptable range, varying from approximately 30% to approximately 57%. In all cases digestibility increased with increasing

mesh number. The material obtained using Process 3 had the maximum digestibility, while that from Process 1 was the least digestible. Process 4, which is considered to be the optimum, yielded materials with average values. For comparison, a digestibility value of 70% or greater is considered to be a good value (Mugerwa and Bwabye 1974) for materials to be used as feeds. The oversize fractions resulting from these processes appear to be acceptable as ruminant feed components, depending upon sales prices.

TABLE 3.
IN VITRO DIGESTIBILITY FOR THE DIFFERENT PROCESSES

Process	In Vitro Digestibility			
	+45 Mesh		+100 Mesh	
	Dry Matter	Organic Matter	Dry Matter	Organic Matter
1	N.A.	N.A.	38.42	36.83
2	35.02	32.65	46.81	44.43
3	44.08	43.56	55.69	52.77
4	28.96	27.71	39.45	38.87

N.A. = Not Available.

SUMMARY CONCLUSIONS

A process which yields a mesquite pod protein concentrate of good quality has been found. The process involves toasting of mesquite pods, followed by passing the pods one time through an Alpine mill, and screening the milled material into fractions. The protein is concentrated in the −100 mesh fraction. As far as is known, no other work is reported in the scientific literature which obtains this type of mesquite product.

The process has a number of advantages: (1) it is simple, since only three steps are required (toasting, milling, sieving); (2) it involves only mechanical procedures; (3) no wet processing is required; and (4) for all of the above reasons, the process is low in costs and energy efficient.

The mesquite pod protein concentrate obtained possesses a number of advantages: (1) it is an extremely fine powder, suitable for many applications; (2) it possesses a light toasted color and a pleasant toasted flavor, both factors which would enhance the organoleptic quality of products developed utilizing the concentrate; (3) it possesses a good protein concentration and reflects an extremely high protein recovery; and (4) the fiber content is nearly half that of whole pods.

The development of this process improves the possibility of utilizing mesquite pods, which grow wild and abundantly in many developing countries, as an inexpensive protein and calorie source.

By-products obtained from the process (coarse and intermediate fractions) may be utilized in ruminant feeds. This increases the value of the process, making it more attractive as an investment alternative in developing countries.

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PARTITION OF VCM IN PLASTICIZED PVC/FOOD SIMULANT SYSTEMS

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ABSTRACT

Partition of Vinyl Chloride Monomer (VCM) between plasticized PVC films and corn oil and between PVC films and water was studied. A specific procedure with predetermined calibration curves has to be followed in order to obtain reliable and reproducible results. At very low VCM levels, the partition coefficient increased with decrease in monomer concentration indicating a preference of the monomer towards the polymer. In plasticized PVC films, the level of plasticization may affect the residual VCM in the film, the rate and extent of monomer migration from the polymeric matrix, as well as the equilibrium monomer distribution between the PVC and the contacting phase.

INTRODUCTION

The migration of Vinyl Chloride Monomer (VCM) from Polyvinyl Chloride (PVC) packages into contacting phases has been subject to many investigations in recent years as a result of the discovery that the monomer is a potential carcinogen, Maltoni and Lefemine (1975).

Daniels and Proctor (1975) studied the extraction of VCM from PVC bottles by several food simulants. They determined the partition coefficients, K_p, in the various systems for the range of initial VCM concentration in the polymer of 100–400 ppm (w/w). For lower VCM concentrations, the partition coefficients were estimated from linear extrapolations of plots relating K_p to concentration. Sato *et al.* (1977) studied the migration of VCM into several food simulants from PVC packages containing various amounts of residual monomer in the range of 1–108 ppm. After five months of storage, considerable amounts of VCM were found in salad oil and soy sauce even when the residual VCM in the package was in the range of 1–5 ppm. Alcoholic liquors packaged in PVC bottles were also

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reported to be contaminated with VCM (Federal Register 1973). The migration of VCM from PVC was also studied by Figge (1972); Chudy and Crosby (1977); Diachenco *et al.* (1977). Morano *et al.* (1977) found a nonlinear relationship between the partition coefficient and the initial VCM concentration in the systems PVC/n-hexane and PVC/vegetable oil. The partition coefficient (defined as the ratio between the equilibrium monomer concentration in the polymer and that in the contacting phase) was found to increase with the decrease in the initial monomer concentration showing a higher preference of the polymer by the monomer at low monomer concentrations. Similar results were found by Kashtock (1977) also working with unplasticized PVC but at lower VCM concentrations.

The migration of a low molecular weight compound from a polymeric matrix depends on the temperature, on the polymer-migrant interaction and the affinity of the migrant for the contacting phase. Thus, the equilibrium distribution of the migrant between phases will be determined by the thermodynamics of the interactions, while the rate of attaining this equilibrium depends on the kinetics. The concentration dependence of the partition coefficient at low monomer concentrations can be described either by a Langmuirian or Freundlich type sorption. Whereas the first type assumes homogeneity of the active sites in the polymer on which the monomer is sorbed, the latter proposed hetergeneous active sites. The dual mode sorption theory proposed by Vieth and Sladek (1965) also predicts a concentration dependent partition coefficient. Therefore, a linear extrapolation of the partition coefficient values obtained at high concentrations to low concentrations is unjustified.

The present work was therefore extended over the previously reported one (Kontaminas *et al.* 1982) to study the partition of Vinyl Chloride Monomer (VCM) between plasticized PVC and food simulant systems. Plasticizers incorporated into PVC change its physical properites, and it can therefore be assumed that the transit and the equilibrium mass transport of residual monomers from the polymer may also be altered.

EXPERIMENTAL MATERIALS

The plasticized PVC films were donated by Reynolds Metal Co., Richmond, Virginia. The films contained the following concentrations of Di-iso-octyl adipate as plasticizer:

PVC film "Type II" - 24%; "SMT" film - 25%; and "XP82" film - 15% (w/w).

The difference between the first two films is that they contained a different combination of plasticizers although the major component in them was Di-iso-octyl adipate and the total concentration was similar. The third film contained a different level of plasticizer.

Distilled water and commercial corn oil packaged in glass bottles were used in the present work as food simulants.

METHODS

Stock solutions of VCM in vegetable oil and in water were prepared daily by direct injection of predetermined amounts of VCM into closed vials containing the simulants.

Analysis of the residual VCM in the film samples was carried out by the FDA procedure (Dennison *et al.* 1978) using gas chromatography/mass spectrometry (GC/MS). A Hewlett Packard model 5990A GC/MS was used with the following operating conditions:

Temperature, injector - 150 °C - column - 150 °C.
Carrier gas (helium) flow rate - 22 mL/min.
E.M. voltage - 3000.
VCM elution time - 1.3 min approximately.

A 180 × 0.6 cm O.D. coiled glass column filled with 80/100 mesh chromosorb 104 (Acrylonitrile-vinylbenzene copolymer, John Manville, Celite Division, Denver, Colorado) was used. The GC/MS, operating in the selected ion mode, monitored the m/e 62 and 64 ions under computer control. For quantification, the m/e 62 ion abundance was used. The linearity and sensitivity of the procedure was determined with carefully prepared solutions of VCM in ethanol.

Partition coefficients for VCM in PVC/oil and PVC/water systems were determined by a headspace analysis using GC/MS operating at the conditions indicated above. A ratio of 0.2:1 PVC:simulant was used (w/w) and the exposed area was approximately 800 cm^2. Six different initial VCM concentrations were used for each of the two systems. For these tests, the PVC films were cut into pieces of 2.5 × 0.6 cm, weighed and inserted into a 26 mL vial. A VCM solution of known concentration was prepared from a stock solution in the appropriate simulant and added to completely fill the vial. The vial was then capped with a teflon faced rubber septum and sealed with an aluminum crimp, care being taken out to leave any free headspace. The sample containing a magnetic stirrer was then left to equilibrate under agitation before VCM concentrations were measured. For decreasing concentrations of VCM (in the ranges of 50–200, 30–105 and 20–50 ppb) in the PVC/oil system, 1, 2 or 4 mL of the oil, respectively, were withdrawn from the vial after equilibrium was reached (the time for obtaining equilibrium was predetermined in preliminary experiments) and injected into a 26 mL closed vial. The vial was heated at 100 °C for 2 h and 2 mL sample of the headspace withdrawn and injected into the GC/MS for VCM determination. Calibration curves were prepared by injecting 2 mL of the

headspace taken from vials containing 1, 2 and 4 mL VCM in oil solutions (of known concentrations) also preheated for 2 h at 100 °C. The VCM concentration in the oil used for partition coefficient determination was calculated from the corresponding calibration curve while the concentration in the plasticized PVC films was calculated by difference.

For the PVC/water system a similar procedure was followed except that the amounts of liquid injected into the 26 mL closed empty vials for headspace analysis were 0.5 mL and 2 mL for the high and low VCM concentrations, respectively. These vials were also preheated for 2 h at 100 °C for headspace analysis and 2 mL of the headspace were injected into the GC/MS.

The VCM concentration in the water and in the PVC films was determined in the same way as for the PVC/oil system.

Some of the methods used in the present work were similar to those applied in a previous study, Kontaminas *et al.* (1982).

In all cases duplicate samples were prepared for each VCM concentration and at least two injections with good reproducibility were made from each partition vial.

RESULTS AND DISCUSSION

The analysis of the PVC films showed no presence of residual VCM for the "TYPE II" and "SMT" films at a detectability limit of 2.6 ppb (w/w -VCM/PVC). The "XP82" film contained 2.8 ppb. A recovery of 70% of the VCM from ethanol (FDA method) based on recovery studies conducted prior to the present analysis was assumed.

In Fig. 1, the partition curves of VCM standard between headspace and corn oil are illustrated for the three amounts of oil in the vial. It can be seen that three separate lines were obtained.

In Fig. 2, the partition curves of VCM standard between headspace and water are given for the two amounts of water in the vial. Again two separate lines were obtained in the same general manner as for the oil. It can therefore be concluded that a specific procedure with predetermined calibration curves has to be followed in order to obtain reliable and reproducible results.

The partition coefficient (K_p) of VCM betwen the PVC films and corn oil as a function of initial VCM concentration is shown in Fig. 3. It can be seen that in all three films there is a nonlinear distribution of VCM between the film and the oil, the monomer favoring the polymer especially at the very low VCM concentration. For clarity, the partition coefficients are also given in Table 1.

In Fig. 4 a similar plot as Fig. 3 is shown for the PVC/water system. The actual values are also summarized in Table 1. In this case, the affinity of the monomer to the polymer is even higher (higher K_p values), as compared to the PVC-oil system. Nonlinear partition of VCM between PVC and contacting phases was also found in a previous study with unplasticized PVC (Kontaminas

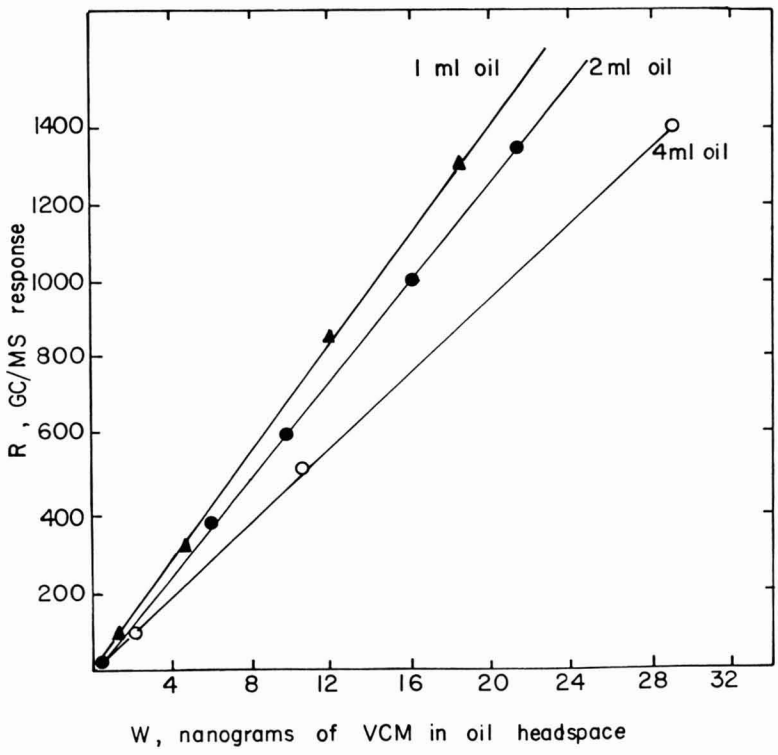

FIG. 1. STANDARD PARTITION CURVES OF VCM BETWEEN HEADSPACE AND CORN OIL AT THREE AMOUNTS OF OIL IN THE VIAL

et al. 1982). In the films "Type II" and "SMT" of the present study, the increase in partition coefficient with the decrease in initial VCM concentration is again clearly seen. However, in the film "XP82" no such concentration effect was noticed and the partition coefficient remained constant throughout the whole studied VCM concentration range. It should be mentioned, however, that this was the only film for which a residual VCM concentration (2.8 ppb) was detected. In addition, this film had also the lowest level of plasticizer. The presence of residual VCM molecules occupying the most active sites in the polymer matrix can probably explain partly the independence of the partition coefficient on initial VCM concentration.

The effect of plasticizer on partial deactivation of active sites was shown by Morano *et al.* (1977) and Kashtock (1977) although at much higher levels of residual VCM than in the present study. It becomes evident from the present study too that the plasticizer level may affect the residual VCM in PVC films as well as the distribution of residual VCM between the polymeric film and the contacting medium.

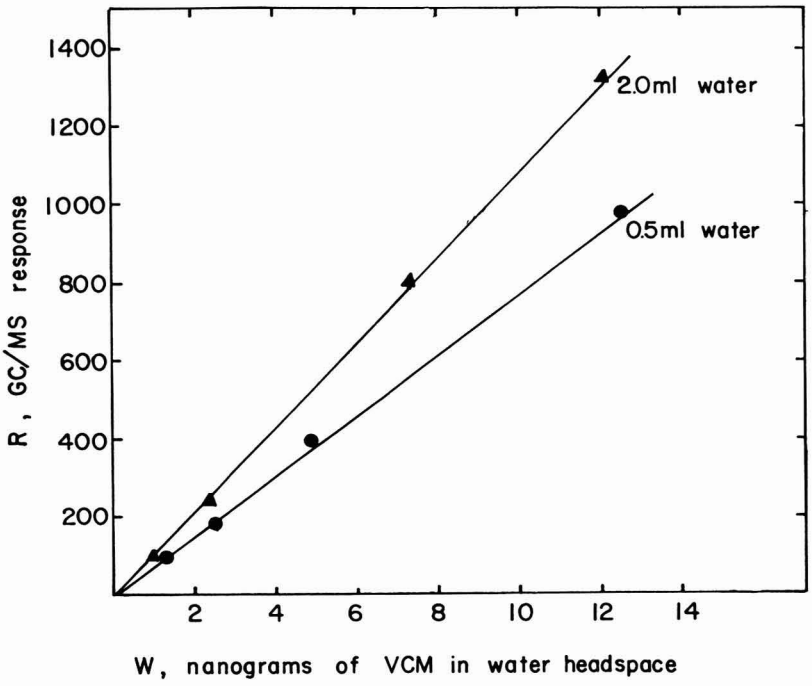

FIG. 2. STANDARD PARTITION CURVES OF VCM BETWEEN HEADSPACE AND WATER AT TWO AMOUNTS OF WATER IN THE VIAL

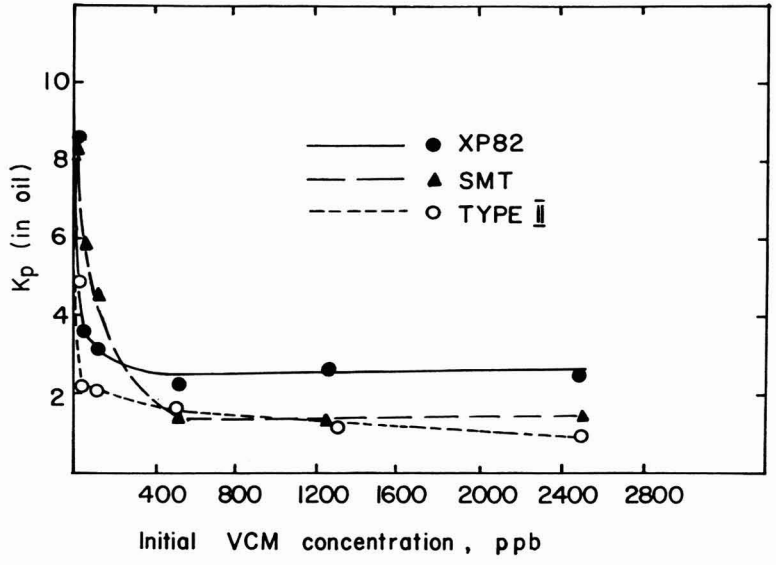

FIG. 3. EFFECT OF INITIAL VCM CONCENTRATION ON THE PVC/CORN OIL PARTITION COEFFICIENT

TABLE 1.
PARTITION COEFFICIENTS OF VCM IN THE DIFFERENT PVC/SIMULANT SYSTEMS

Type of Film	Contacting Phase	Initial VCM Concentration C_{pol}	Partition Coefficient K_p
Type II	Corn oil	25.	4.9
		51.	2.2
		128.	2.1
		510.	1.6
		1300.	1.2
		2500.	0.9
"SMT"	Corn oil	25.	8.4
		51.	5.8
		127.	4.5
		510.	1.5
		1250.	1.3
		2510.	1.4
"XP82"	Corn oil	25.	8.5
		51.	3.6
		126.	3.1
		510.	2.7
		1250.	2.3
		2490.	2.6
"XP82"	Distilled water	31.	16.7
		63.	14.5
		157.	9.1
		313.	9.0
		1200.	5.5
		2300.	6.5
"SMT"	Distilled water	31.	40.4
		63.	22.2
		151.	23.0
		307.	17.6
		1170.	6.4
		2330.	7.4
"XP82"	Distilled water	31.	5.8
		63.	5.5
		157.	5.3
		313.	6.4
		920.	5.4
		1530.	6.4

To conclude, it was shown that a very low monomer concentrations the monomer affinity for the polymer as compared to that for the contacting phase becomes very high and a linear extrapolation of the K_p values from higher VCM concentrations is erronous and unjustified. This strengthens once again our "effective zero" concept outlined in previous publications Gilbert (1976); Gilbert *et al.* (1980); Miltz *et al.* (1980); Orr *et al.* (1981); Khalil *et al.* (1983) proposing that a low enough monomer concentrations and especially at low (room)

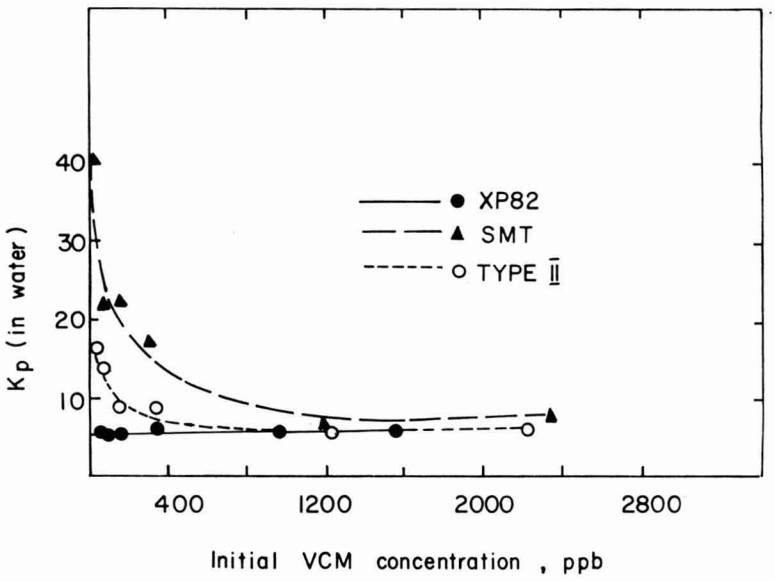

FIG. 4. EFFECT OF INITIAL VCM CONCENTRATION ON THE PVC/WATER PARTITION COEFFICIENT

temperatures no actual monomer migration to a contacting phase may occur since the monomer is tightly bound to the most active sites in the polymer matrix. Also, in plasticized PVC films the level of plasticization may affect the residual VCM in the film, the propensity of the monomer to migrate from the polymeric matrix, and the monomer distribution between the PVC and the contacting phase.

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COMPUTER CODES AND THEIR APPLICATION

ALGORITHM FOR QUALITY CONTROL CHARTS FOR VARIABLES USING MICROCOMPUTERS[1]

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INTRODUCTION

Statistical quality control is the term used for the application of statistical methods to quality assurance programs. These methods involve the collection, analysis, interpretation and presentation of data which aid in the maintenance of the acceptable quality of a product (Powers and Rao 1985). One statistical tool used in quality assurance programs are the control charts for variables. These control charts consist of the average-range charts and the average-standard deviation charts. Use of the control charts can help determine whether variability in a product is due to natural variation or assignable causes (Duncan 1952). The objective of this work was to develop a computer algorithm which could accurately calculate and graphically represent the control charts using a microcomputer.

THEORETICAL CONSIDERATIONS

Construction of average-range charts involves the collection of measurement data for several samples. The average and range for each sample is calculated, and the grand average and average range are calculated for all the samples. The average-standard deviation charts are constructed in a similar manner. The average and standard deviation of each sample is calculated and the grand average and average standard deviation are calculated for all the samples. The control limits for the four charts are calculated according to the following formulas:

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Average-Range Charts:

Upper control limit for $\bar{X}$ chart $= \bar{\bar{X}} + A_2\bar{R}$

Lower control limit for $\bar{X}$ chart $= \bar{\bar{X}} - A_2\bar{R}$

Upper control limit for R chart $= D_4\bar{R}$

Lower control limit for R chart $= D_3\bar{R}$

Average-Standard Deviation Charts:

Upper control limit for $\bar{X}$ chart $= \bar{\bar{X}} + A_1\,\bar{\sigma}$

Lower control limit for $\bar{X}$ chart $= \bar{\bar{X}} - A_1\,\bar{\sigma}$

Upper control limit for σ chart $= B_4\,\bar{\sigma}$

Lower control limit for σ chart $= B_3\,\bar{\sigma}$

The values for A_2, D_4, D_3, A_1, B_4 and B_3 can be found in most texts on statistical quality control, and are based on the sample size (Grant and Leavenworth 1980). They are stored in the computer program as arrays. The central lines for each of the four charts are the values of $\bar{\bar{X}}$, $\bar{R}$, $\bar{\bar{X}}$ and $\bar{\sigma}$, respectively. The values of the individual sample groups are plotted on the charts along with the control limits and the central lines. An example of the format used for graphical representation of control charts is shown in Fig. 1. If all of the points that are plotted fall inside the control limits on the charts, the process is said to be "in control". Conversely, if any of the plottings fall outside of the control limits the process is said to be "out of control". The approximate probability of a plotted point falling outside of the control limits due to assignable cause is 99 in 100 (Rao and Griffith 1977). Therefore, if a plotting does fall outside of the calcualted control limits it is assumed to be caused by a problem in the process that needs to be corrected.

COMPUTER ALGORITHM

A flow chart illustrating the algorithm for the computer program developed in this work is presented in Fig. 2. The source code was written in PASCAL and was compiled to machine language code on an IBM personal computer. The program can be assessed directly from the operating system of the computer by typing the name of the program at the DOS prompt. The program first prompts the user for input of previously calculated central lines, sample size and number of samples, if desired. This can be done via keyboard or disk file. The user is then prompted for the current data. This may also be input from the keyboard or from a disk file. The user inputs the number of samples, sample size, and the data for each sample. The number of samples and sample size are currently limited to a maximum of one hundred each, though these values could be increased if needed by redefining the arrays in the program source code. The program allows the user to review and/or correct the data if necessary. At this point, the program performs the calculations detailed in the above section and displays the values

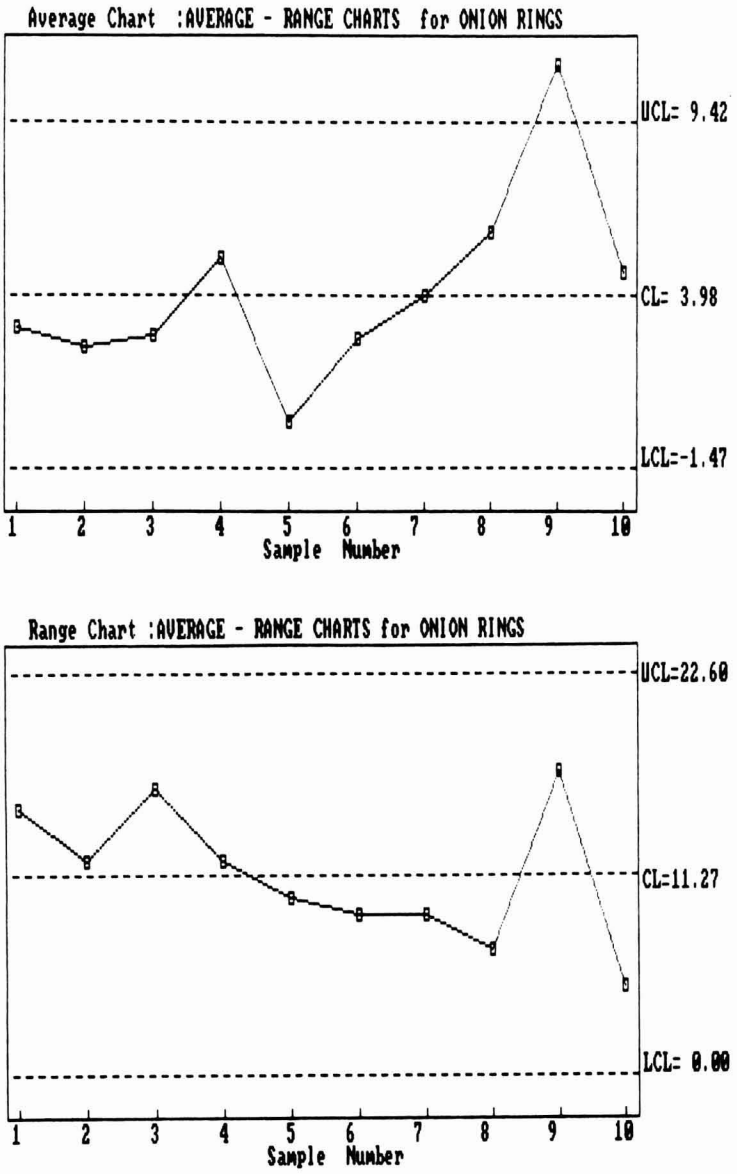

FIG. 1. COMPUTER GENERATED GRAPHS OF $\overline{X}$ AND R CHARTS

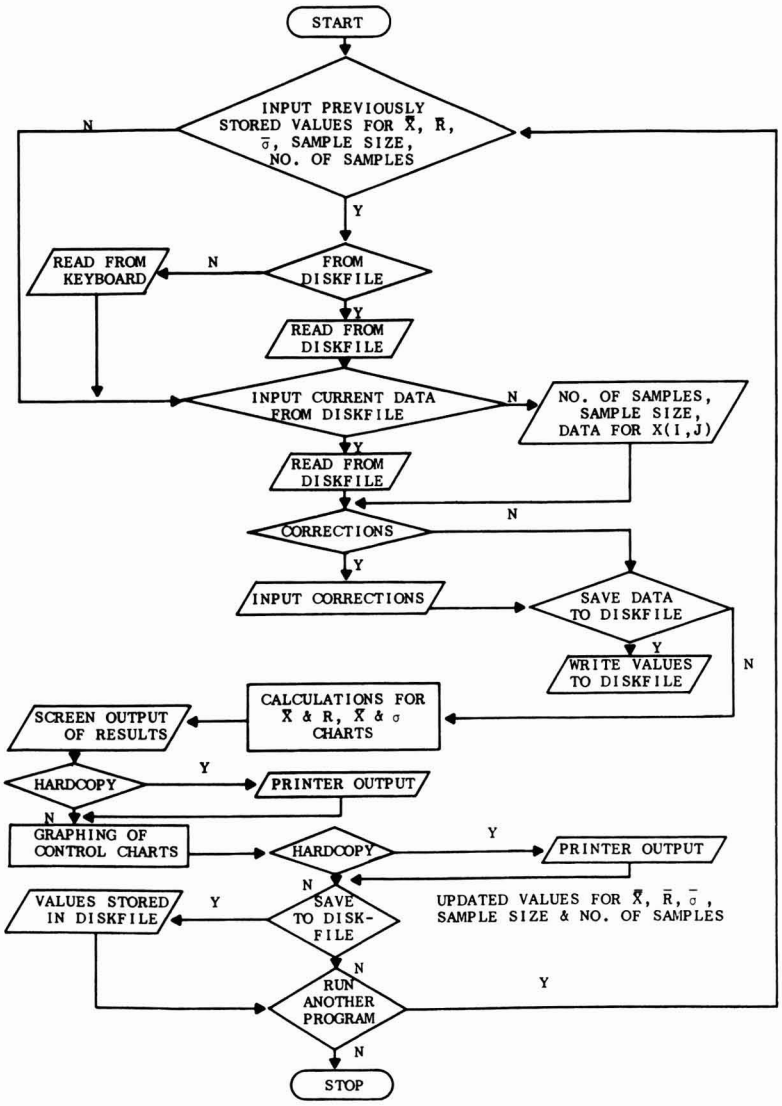

FIG. 2. FLOW CHART OF THE ALGORITHM FOR DETERMINING QUALITY CONTROL CHARTS FOR VARIABLES

for the control limits and central lines on the screen. The averages of the samples (average, range and standard deviation) are also displayed on the screen and any sample groups found to be outside of the control limits are marked with an asterik. These results will be output to the printer if the user has chosen the print option. The next step is the display of the control charts on the screen, one at a

time, with an option for a hardcopy available (Fig. 1). The next two prompts allow the user to store the updated values of $\bar{\bar{X}}$, $\bar{R}$, $\bar{\sigma}$, number of samples used and sample size to a disk file, which allows future calculations of control limits to be based on previous and present samples, and also to store the data on individual samples to a separate disk file. Typical printer output of the computer session is shown in Fig. 3.

```
 CONTROL CHARTS FOR MEASUREMENTS for : ONION RINGS     2-25-86

 Measurements from previous runs of program:

XDBAR =   3.94          Sample size = 6
 RBAR =  11.29
 SBAR =   3.79     Number of samples = 50

An * following a number means that the data is out-of-control

 SAMPLE              MEAN              RANGE              STD
sample #  1          3.00              15.00              4.65
sample #  2          2.33              12.00              4.68
sample #  3          2.67              16.00              5.76
sample #  4          5.17              12.00              3.98
sample #  5         -0.04              10.00              3.38
sample #  6          2.63               9.00              2.86
sample #  7          4.00               9.00              2.94
sample #  8          6.00               7.00              2.31
sample #  9         11.33*             17.00              5.34
sample # 10          4.67               5.00              1.70

Average of            4.17              11.20              3.76
samples

GRAND AVERAGE         3.98              11.27              3.79

                AVERAGE - RANGE CHARTS
 Average Chart

 Upper Control Limit          9.42
 Central Line                 3.98
 Lower Control Limit         -1.47

 Range Chart

 Upper Control Limit         22.60
 Central Line                11.27
 Lower Control Limit          0.00

          AVERAGE - STANDARD DEVIATION CHARTS
 Average Chart

 Upper Control Limit          9.32
 Central Line                 3.98
 Lower Control Limit         -1.36

 Standard Deviation Chart

 Upper Control Limit          7.46
 Central Line                 3.79
 Lower Control Limit          0.11
```

FIG. 3. TYPICAL PRINTOUT USING THE COMPUTER PROGRAM FOR CONTROL CHARTS

CONCLUSIONS

The computer program developed in this work can be used to facilitate statistical analysis of quality control data. The program can output the results to a printer in a matter of minutes, which is a considerable time savings over hand drawn control charts. As microcomputers become available to quality control personnel, computer programs such as this can become a valuable tool in a quality assurance program. The program is currently in use by several food industries in the state of Georgia, and is readily available from the authors.

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