

AN ABSTRACT OF THE THESIS OF

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Title: FROZEN SHELF-LIFE CHARACTERISTICS OF CONDENSED

PHOSPHATE TREATED PACIFIC SHRIMP MEAT (PANDALUS

JORDANI)

Abstract approved: _____

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The effect of the application of condensed phosphate (Brifisol D-510, commercial mixture of sodium tripolyphosphate and sodium hexametaphosphate) to round shrimp on the yield and frozen shelf-life characteristics of cooked meat was investigated. Condensed phosphate retarded protein solubilization and increased the water-holding capacity of meat through steam precooking markedly improving yield. The effectiveness of condensed phosphate application was enhanced by the post-catch degradative changes occurring in the shrimp musculature proteins during ice storage. Cooked meat yields (wet wt.) for phosphate treated round shrimp after two, four and seven days ice storage were $30.70 \pm 0.51\%$, $31.22 \pm 0.03\%$ and $29.21 \pm 0.23\%$, while the yields from control samples were $26.52 \pm 0.18\%$, $27.14 \pm 0.01\%$ and $23.85 \pm 0.09\%$, respectively.

The phosphorus contents of cooked meat from control shrimp were 842.54, 726.08 and 577.74 mg $P_2O_5/100$ gm (wet wt.) after 2, 4 and 7 days storage in ice. Phosphate treatment produced an increase of 91.20, 134.34 and 184.68

mg P_2O_5 /100 gm (wet wt.) over respective control samples. The loss of solid material retarded by condensed phosphate pretreatment and increased as ice storage was extended was inversely proportional to the iron and copper contents in cooked shrimp meat.

Initial levels of tyrosine, trimethylamine oxide, trimethylamine and dimethylamine in cooked meat reflected the quality of round shrimp as mediated by ice storage. Differences were related to drip loss and bacterial and enzymic degradation. The level of tyrosine in cooked shrimp meat did not significantly change with respect to frozen storage time. A higher level of trimethylamine oxide was retained in the meat from phosphate treated shrimp than respective control samples. trimethylamine oxide decomposed during ice and frozen storage; decomposition with respect to frozen storage time followed an exponential function. Differences in initial levels of trimethylamine in cooked meat were presumably related to the bacterial load in round shrimp. Condensed phosphate treatment reduced the trimethylamine contents of cooked meat. Dimethylamine levels increased during ice storage of the raw shrimp and frozen storage of the cooked meat which supports the existence of a non-enzymatic mechanism, but did not rule out an enzymatic mechanism in the raw tissue. Dimethylamine was formed in cooked meat according to an exponential function; the rate of formation was inversely related to the magnitude of solids lost through precooking. Dimethylamine was formed more rapidly

in frozen cooked meat from fresh and phosphate treated shrimp.

Condensed phosphate had a significant effect on retarding toughening during frozen storage as measured by shear press. Shear press values were correlated with dimethylamine content which is co-produced with formaldehyde.

In all sensory evaluations, phosphate treated shrimp yielded cooked meat that possessed a higher quality than respective control samples. Sensory quality of cooked meat was slightly different at two and four day ice storage, but flavor panels showed a significant degradation after seven days ice storage. Color, flavor and overall desirability scores from shrimp were not correlated with frozen storage. Texture and juiciness scores did not significantly change as frozen storage was extended. The frozen storage stability of cooked meat from condensed phosphate treated shrimp did not appear to differ from that of non-treated.

FROZEN SHELF-LIFE CHARACTERISTICS OF
CONDENSED PHOSPHATE TREATED
PACIFIC SHRIMP MEAT
(PANDALUS JORDANI)

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TABLE OF CONTENTS

| | |
|--|----|
| INTRODUCTION | 1 |
| LITERATURE REVIEW | 3 |
| EXPERIMENTAL | 11 |
| Processing Procedure and Meat Yield | 11 |
| Initial Analyses | 12 |
| Determination of Moisture and Phosphorus Contents | 12 |
| Determination of Iron Content | 12 |
| Determination of Copper Content | 13 |
| Storage Analyses | 14 |
| Extraction Procedure | 14 |
| Determination of Tyrosine | 14 |
| Determination of TMAO and TMA | 15 |
| Determination of DMA | 15 |
| Objective Texture Measurement | 16 |
| Sensory Evaluations | 17 |
| RESULTS AND DISCUSSION | 18 |
| Effect of Condensed Phosphate Pretreatment on Cooked Meat Yield | 18 |
| Changes in Phosphorus, Iron and Copper Contents | 20 |
| Changes in Tyrosine Content | 20 |
| Changes in TMAO Content | 22 |
| Changes in TMA Content | 28 |
| Changes in DMA Content | 32 |
| Changes in Levels of Objective Texture Measurement | 35 |
| Sensory Evaluations of the Quality of Frozen Cooked Shrimp Meat | 41 |
| SUMMARY AND CONCLUSIONS | 59 |
| BIBLIOGRAPHY | 61 |

LIST OF FIGURES

| Figure | Page |
|--|------|
| 1. Diagrammatic representation of work diagrams | 16 |
| 2. Mean color scores of frozen cooked shrimp meat (condensed phosphate treatment) | 49 |
| 3. Mean color scores of frozen cooked shrimp meat (control) | 50 |
| 4. Mean texture scores of frozen cooked shrimp meat (condensed phosphate treatment) | 51 |
| 5. Mean texture scores of frozen cooked shrimp meat (control) | 52 |
| 6. Mean juiciness scores of frozen cooked shrimp meat (condensed phosphate treatment) | 53 |
| 7. Mean juiciness scores of frozen cooked shrimp meat (control) | 54 |
| 8. Mean flavor scores of frozen cooked shrimp meat (condensed phosphate treatment) | 55 |
| 9. Mean flavor scores of frozen cooked shrimp meat (control) | 56 |
| 10. Mean overall desirability of frozen cooked shrimp meat (condensed phosphate treatment) | 57 |
| 11. Mean overall desirability of frozen cooked shrimp meat (control) | 58 |

LIST OF TABLES

| Table | Page |
|---|------|
| 1. Meat yield and moisture content of cooked shrimp meat | 19 |
| 2. Mean levels of phosphorus, iron and copper contents in cooked shrimp meat | 21 |
| 3. Mean levels of tyrosine (ug/mg) in frozen cooked shrimp meat | 23 |
| 4. Factorial analysis of tyrosine in frozen cooked shrimp meat | 24 |
| 5. Mean levels of TMAO (ug/gm) in frozen cooked shrimp meat | 26 |
| 6. Factorial and regression analyses of TMAO in frozen cooked shrimp meat | 27 |
| 7. Mean levels of TMA (ug/gm) in frozen cooked shrimp meat | 30 |
| 8. Factorial and regression analyses of TMA in frozen cooked shrimp meat | 31 |
| 9. Mean levels of DMA (ug/gm) in frozen cooked shrimp meat | 33 |
| 10. Factorial and regression analyses of DMA in frozen cooked shrimp meat | 34 |
| 11. Mean levels of objective texture measurement of frozen cooked shrimp meat | 36 |
| 12. Factorial analyses of objective texture measurements of frozen cooked shrimp meat | 37 |
| 13. Regression the values of objective texture measurement on frozen storage | 38 |
| 14. Regression analysis of total work on DMA content | 40 |
| 15. Mean color scores for frozen cooked shrimp meat | 44 |
| 16. Mean texture scores for frozen cooked shrimp meat | 45 |

LIST OF TABLES (continued)

| Table | Page |
|--|------|
| 17. Mean juiciness scores for frozen cooked shrimp meat | 46 |
| 18. Mean flavor scores for frozen cooked shrimp meat | 47 |
| 19. Mean overall desirability scores for frozen cooked shrimp meat | 48 |

FROZEN SHELF-LIFE CHARACTERISTICS OF CONDENSED PHOSPHATE
TREATED PACIFIC SHRIMP MEAT
(PANDALUS JORDANI)

INTRODUCTION

Pretreating round shrimp with condensed phosphate solution prior to steam precooking and subsequent mechanical peeling enhances water-holding capacity, increases shell removal efficiency and reduces meat loss (Nouchpramool, 1980). Crawford (1980) indicated that condensed phosphate interacted with the proteins of shrimp musculature to retard their solubilization and loss during steam precooking.

Nouchpramool (1980) reported that the degree of protein-polyphosphate interaction was enhanced by the degradative process occurring during ice storage. Post-catch storage of shrimp resulted in a considerable reduction of meat yield but a condensed phosphate pretreatment could markedly retard meat yield loss with respect to storage.

The use of condensed phosphate is now used widely by the shrimp industry in the Pacific Northwest. Reliable quality evaluations are still needed by the shrimp processing industry and regulatory agencies to insure the quality and frozen shelf-life of cooked shrimp meat derived from round shrimp treated with condensed phosphate. This investigation was designed to evaluate the effect of condensed phosphate application. Chemical, objective texture and sensory changes in cooked shrimp meat derived from condensed

phosphate treated round shrimp held in ice storage for various periods of time were determined during extended frozen storage. The interrelationships of phosphate treatment, round shrimp ice storage and frozen cooked meat storage were evaluated.

LITERATURE REVIEW

Quality changes of seafoods are generally considered to result from the combined action of enzymes from either tissue or contaminating microorganisms, chemical alteration and physical handling (Fieger and Friloux, 1954; Fieger et al., 1958). Deterioration caused by microorganisms is mainly due to the formation of compounds which impart off odors, colors and flavors. Bacterial growth in frozen seafoods is not a problem because at temperature below -9°C , the activity of marine bacteria is largely inhibited. The influence of freezing on the enzymes secreted from marine bacteria, however, has not been thoroughly investigated (Slavin, 1968).

Degradation by the action of bacteria or in situ enzyme systems leads to marked alteration in the content of various chemical parameters in seafoods. Changes in pH (Bailey et al., 1956; Luna, 1971), total nitrogen, non-protein nitrogen, free amino acid (Velankar and Govinadan, 1957, 1958; Ganon and Fellers, 1958), volatile acid (Fieger and Friloux, 1954), indole (Duggan and Strasburger, 1946) and carotenoid (Collins and Kelley, 1960; Kelley and Harmon, 1972) content have a close relationship with quality seafoods.

Castell et al. (1970) reported that the change of trimethylamine (TMA) during ice storage could be used as an index of seafoods quality. Formation of TMA in seafoods has been linked to the action of bacterial enzymes, since marine

microorganisms can convert trimethylamine oxide (TMAO) to TMA (Budd and Spencer, 1968). Amano and Yamada (1964) have suggested from their investigation of gadoid fish the possibility of two completely different systems for the reductive degradation of TMAO. One system proposed the bacterial or the exogenous enzymatic reduction of TMAO to TMA. The second system involved the endogenous enzymatic reduction of TMA to dimethylamine (DMA) and formaldehyde (FA).

Fieger and Friloux (1954) indicated that TMA levels in iced shrimp were only of value to indicate whether or not spoilage had occurred. Iyengar et al. (1960) reported that the TMA levels were unreliable and had a limited usefulness as indices of quality for ice stored shrimp. Flores and Crawford (1973) found an increase of TMA levels in intact shrimp during ice storage, but the magnitude of change was not significant and could not be used as a precise index of quality.

Predominantly, the literature ascribes the formation of DMA to the action of endogenous tissue enzyme(s) on TMAO. Presumably these enzyme(s) directly utilize the TMAO as substrate to form DMA and FA (Amano, 1964; Tokunaga, 1964; Tokunaga, 1970; Castell et al. 1970; Tokunaga, 1974). Investigations with fish muscle are not nearly as definitive. Evidence indicates the activity for the formation of DMA was severely reduced in muscle that had been heated in excess of 88°C (Tokunaga, 1964; Castell et al., 1971; Lall et al.,

1975). It is clearly demonstrated, however, that TMAO can be degraded to DMA and FA by chemical reactions (Lecher and Hardy, 1948; Sundsvall et al., 1969). Recently, Spinelli and Koury (1979) reported that DMA rapidly formed in heat-processed dry fish muscle and that several chemical compounds and ionic constituents could easily convert TMAO to DMA. Sundsvold et al (1969a and 1969b) reported that high levels of TMAO in raw and fresh cooked shrimp were converted to TMA, DMA and FA after canning and storage. The addition of reduced iron, copper sulfate and titanous chloride to the canned product accelerated the reduction of the TMAO with subsequent formation to TMA, DMA and FA during storage. Flores and Crawford (1973) reported the DMA and FA levels increased rapidly in a parallel manner in raw shrimp and cooked meat samples during ice storage and suggested that the determination of DMA and FA can be used as a sensitive test that could better reflect the organoleptic quality of shrimp meat. Castell et al (1970) found that in shrimp muscle there was no reduction of TMAO to DMA and FA during frozen storage.

Several investigation showed that tyrosine levels increased during frozen storage and became most evident when advanced spoilage had taken place (Tarr and Bailey, 1939; Vaisey, 1956). Flores and Crawford (1973) reported that the tyrosine level in the cooked shrimp meat generally increased during the storage period and pointed out that a considerable

amount of tyrosine is probably lost during the cooking process.

Seafoods in frozen storage undergo change in odor, color, flavor and texture. Color and flavor changes resulting from the oxidation of oils and pigments are very important in seafoods held in frozen storage, particularly in species of fat fish. The development of toughness can also be a significant problem in fish held in frozen storage.

Dyer (1954) indicated that changes in texture may be associated with the denaturation of proteins. Connell (1964) pointed out that two principal theories had been set forth to explain the cause of protein denaturation during frozen storage: (1) concentration of solutes, especially inorganic salts, to a point during freezing where they damage the protein in stored fish, or (2) lipid hydrolysis. The salt-denaturation theory assumes that exposure to salts, which become concentrated as water is progressively frozen out during the lowering of storage temperature to below 0°C, causes direct damage to protein. The lipid hydrolysis theory comes from an observation by Dyer (1951) that during frozen storage the increase in free fatty acid content parallels protein damage as measured by a decrease in protein extractability. Anderson et al. (1956) proposed that the denaturation of fish muscle protein induced by frozen storage was due to electrostatic interaction between protein and fatty acids.

Mihalyi (1963) indicated that the FA formed during the reduction of TMAO to DMA might be interacting with myofibrillar proteins in a manner similar to the cross-linking with bovine fibrinogen. The interaction of FA with myofibrillar protein could explain, in part, the undesirable textural change that occur during frozen storage of Pacific hake.

Szezsniak and Kleyn (1963) reported that the consumer is highly conscious of meat texture and indicated that this factor may be even more important than flavor. For this reason, extensive studies have been carried out to develop methods of measuring tenderness and relating it to the eating quality of meat. Lehman (1907) was the first to report the use of mechanical measure of meat tenderness. Kramer and Twigg (1959) described an instrument called the shear press. It was developed with the idea that it could be used for several purposes, like measurement of shearing, cutting, pressing and penetrating for a variety of food, both raw and cooked. A more recent model, Allo-Kramer shear press, is available for measuring the texture characteristics of food products. Sidwell and Decker (1959) mentioned that the curves plotted by shear press are good indications of tenderness and also each product had its own particular curve. Shannon et al. (1957) reported a correlation of 0.86 between shear press values and organoleptic panel scores of poultry meat, and Wise (1957) indicated a correlation of 0.89 between results obtained by a chew panel and Kramer shear

values. Bailey et al. (1962) confirmed that the correlation values obtained between shear press and sensory analyses of beef steaks with grades and cuts were generally significant or approaching significant.

The phosphates, and especially the polyphosphates, have been found to prevent or retard the physical changes of stored seafoods. A number of investigators reported that the addition of polyphosphates to seafoods increased tenderness of the stored products. Sen et al. (1961) indicated that addition of sodium hexametaphosphate (SHMP) to curing salts used in preparation of dried-salt cured fish softened the texture making the fish less tough. Garnatz et al. (1949) found that the tenderness of cooked and frozen shrimp was increased to a significant degree by treating them with sodium and potassium phosphates. Love and Abel (1966) pointed that polyphosphates preventing the dehydration of fish muscle which leads to toughening was due to the solubilization of certain proteins in the fish surface tissue.

Alibright and Wilson Ltd. (1961) patented the treatment of fish prior to freezing with polyphosphate to prevent the loss of moisture, soluble protein and minerals. MacCallum et al. (1964) demonstrated that the muscle proteins of cod were not split or hydrolyzed by the phosphates, indicated that phosphate dips did not increase the fish muscle proteins solubility. A further report from the Torry research station (1968) suggested that the polyphosphates

are highly effective in reducing or preventing escape of fluid from fish fillet during storage. The effect was through swelling of the surface cells of the fillets to eliminate extracellular spaces through which the fluids could exude from the interior of the fillets. Phosphates have little or no effect on good quality fish, but do reduce weight loss and improve quality through fluid retention in poorly processed fish.

Collins (1960) found that ice storage of round shrimp facilitated the machine peeling operation, but resulted in lower meat yield. Chao (1979) reported that the degradation of shrimp connective tissue attaching the musculature to the shell during ice storage was directly responsible for enhancing the shell removal function of mechanical peelability. Lapeyre (1968) reported that cooking whole shrimp prior to machine peeling improved the peelability and also found that heat pretreatment induced the formation and accumulation of a fluid and moisture zone between the muscle and shell of the shrimp body.

Nouchpramool (1980) indicated that condensed phosphate (6%) pretreatment coupled with short steam precooking (90 sec.) for shrimp prior to mechanical peeling produced superior cooked meat yield and retained higher moisture content. The increase in cooked meat yield and associated water-holding capacity obtained by condensed phosphate pretreatment might result from two mechanisms: (1) Interaction of polyphosphate

with protein matrix of the sub-cuticle (collagen-like proteins) and other proteins lead to an increase in the solubility of the proteins. These solubilized proteins then gelatinized at the surface sealing it to prevent the loss of fluid and soluble solid material resulting in yield improvement through steam precooking. (2) Complexing of collagen-like proteins markedly reduced their susceptibility toward heat solubilization.

EXPERIMENTAL

Processing Procedure and Cooked Meat Yield

A lot of (approximately 172 Kg) of less than one day old Pacific shrimp was obtained from commercial plants in Astoria, Oregon. Shrimp were divided into sub-lot quantities based upon expected yield that would provide an ample cooked meat sample. Sub-lots were transferred to aluminum pans equipped with drainers, iced and stored at 3.3°C (38°F). Enough of the sub-lot samples were stored to provide duplicate lots for control (water) and condensed phosphate treatment at 2, 4 and 7 days ice storage post-catch.

The experimental solution, 6% condensed phosphate (Brifisol D-510) and water, were prepared one day prior to processing and cooled to 3.3°C (38°F). Samples were briefly deiced in water, drained for 10 minutes and weighed for meat yield calculation. Deiced shrimp were treated with two times their weight of experimental solution for 10 minutes and drained for 5 minutes.

Shrimp were precooked in steam at 101°C in a one body layer thickness for 90 sec., exposed to a brief water spray and peeled utilizing a laboratory scale mechanical peeler. Remaining shell was removed by hand, and the weight of clean meat recorded. Shrimp meat was packed in styrofoam containers and frozen overnight at -34.4°C (-30°F). After freezing, the containers were vacuum sealed in moisture-proof film and

stored at -17.7°C (0°F) for 11 months.

Initial Analyses

Determination of Moisture and Phosphorus Contents

Moisture content was determined according to the method described by A. O. A. C. (1970). Frozen cooked shrimp meat (100 gm) was thawed at 3.3°C (38°F) and the entire contents including the resulting drip were collected in a blender and homogenized into paste. Homogenized samples (5 gm) were weighed into porcelain crucibles in duplicate, dried in an oven at 110°C overnight (8 hours) and cooled in a dessicator. Weight loss was reported as percent moisture content.

After determining moisture content, dried samples were charred slowly with a gas flame and ashed at 550°C overnight (8 hours). The ash was transferred into a 25 ml volumetric flask by washing thrice; first with ≥ 1 ml 6N HCl and then with ≥ 1 ml of distilled water. The flask was diluted to volume just prior to analysis.

Total phosphorus was determined according to procedures described by Bartlett (1959). Phosphorus contents were reported as P_2O_5 in mg/100 gm shrimp meat (wet wt.)

Determination of Iron Content

The dry-ashing procedure and analysis by atomic absorption spectrophotometer (AAS) were used respectively for moisture correction and iron content determination (Gordon,

1977).

Ten gram homogenized samples were dried 12 hours at 110°C for moisture correlation. Samples were charred with an open gas flame until thoroughly carbonized and then ashed at 550°C for another 12 hours. The ash was transferred into a 25 ml volumetric flask with three 1 ml 6N HCl and diluted to 25 ml total volume with distilled water.

The absorption of diluted solution was determined using a Perkin-Elmer model 403 AAS with a single element hollow cathode lamp. Absorption was measured at 252.7 nm (Perkin-Elmer corp., 1973). Iron levels were determined from the calibration curve prepared from an iron standard (100 ug Fe/ml, Harleco, 60th and Woodland Ave., Philadelphia, PA 19143) diluted in distilled water.

Determination of Copper Content

Copper content was determined by AAS using a Perkin-Elmer model 403 and the dry-ashing procedure was used for moisture correction (Baker, 1973).

Ten gram homogenized samples were dried 12 hours at 110°C in porcelain crucibles for moisture correlation. Samples were charred with an open gas flame until thoroughly carbonized and then ashed at 550°C for 3 hours. Crucibles were allowed to cool. The residue was treated with 4-6 drops of 5N HNO₃ and dried on a hot plate. Four ml 6N HCl was added, then heated gently to dissolve ash. The dissolved

solution was quantitatively transferred to 25 ml volumetric flask with 0.1N HCL and diluted to volume with 0.1N HCl.

Absorption of diluted solution was measured at 324.7 nm (Perkin-Elmer corp., 1973). Copper levels were determined from the calibration curve prepared from copper standard (1000 ug Cu/ml, Scientific Products, McGaw Park, Illinois 60085) diluted in distilled water.

Storage Analyses

Extraction Procedure

Thawed shrimp meat (100 gm) was homogenized in a blender for 5 minutes. Homogenized meat (25 gm) was extracted with 5% trichloroacetic acid (1:4) in a blender for 5 minutes. The homogenate was held for at least 30 minutes at 2-3°C and then filtered through a Whatman 2V filter paper. The filtrate was collected in vials and stored at -17.7°C (0°F) prior to analysis.

Determination of Tyrosine

Tyrosine was determined according to the method described by Ceriotti and Spandrio (1957). To 5 ml samples of solution containing tyrosine, 1 ml of 0.1% α -nitroso- β -naphthol solution, 0.5 ml of 2.5N HNO₃ and 1.5 ml HCl (s. p. 1.19) were added. The mixture was shaken well, heated in boiling water for exactly 2 minutes, and then cooled immediately under running water. Tyrosine was estimated from a calibra-

tion curve based upon the absorption of a series of standardized tyrosine solutions at 510 nm.

Determination of TMAO and TMA

TMA was determined using the picric acid procedure (Dyer, 1945) modified by the substitution of KOH for K_2CO_3 . The levels of TMA were estimated from a calibration curve based upon the absorption of a series of solutions of trimethylamine hydrochloride at 410 nm previously standardized by a semi-micro Kjeldahl procedure (A. O. A. C. 1970).

TMAO was determined using a modification of the procedure of Yamagata et al. (1969) involving the reduction of TMAO to TMA by adding $TiCl_3$. The subsequent analysis for TMA content followed the method described above. The difference between the "total TMA" obtained by this method and the original TMA was TMAO content, expressed as TMA. To obtain the TMAO concentration, the result was multiplied by a factor of 1.27.

Determination of DMA

A modified method of Dyer and Mounsey (1945) was used to determine DMA. Argaiiz (1976) found an interference in the application of this method to shrimp which prevented the formation of the dimethyl-dithiocarbamate salt and yield erroneous results. To correct the problem, Argaiiz (1976) showed the steam distillation into a slightly acidic solution removed the interfering substance. A 10 ml sample of TCA

extract was introduced into a semi-micro Kjeldahl still with 45% KOH. Approximately 25 to 30 ml of distillate was collected in 10 ml of 0.75N HCl and then brought to 50 ml with distilled water. A 10 ml sample was used for the analysis of DMA. The level of DMA was estimated from a calibration curve based upon the absorption of a series of solutions of dimethylamine hydrochloride at 440 nm previously standardized by a semi-micro Kjeldahl procedure (A. O. A. C. 1970).

Objective Texture Measurement

Objective texture measurements were carried out by using Allo-Kramer shear press. The 150 gm sample of thoroughly thawed shrimp meat was used for this measurement. The work diagrams obtained from this analysis, which is diagrammatically represented in Figure 1, were later measured for the following: maximum force and total work. The maximum force (pound) was obtained from the distance of BC (inch) multiplied by 100 (pound-inch). The total work (inch-pound) was obtained from the area of ABC (sq. inch) multiplied by 100 (pound/inch).

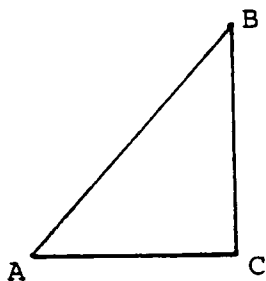


Figure 1: Diagrammatic representation of work diagrams

Sensory Evaluation

Flavor panels were carried out using 10 staff members of the Department of Food Science in Corvallis, Oregon. Frozen samples were thawed out overnight at refrigerator temperature and served in coded cups to judges. Panelists were asked to judge the sample for color, texture, flavor, juiciness and overall desirability on a 9 point scale, ranging from 9 "extremely desirable" to 1 "extremely undesirable".

Evaluations were carried out in duplicate at 11, 107, 200, 283 and 330 days frozen storage, respectively.

RESULTS AND DISCUSSION

Effect of Condensed Phosphate Pretreatment on Cooked Meat Yield

Pacific shrimp (Pandalus jordani) obtained from commercial plants in Astoria was used to evaluate the effect of condensed phosphate pretreatment (6%) at low temperature (3.3°C; 38°F) prior to steam precooking (101°C, 90 sec.) and subsequent mechanical peeling. The influence of extended ice storage on meat yield was also investigated.

The increment of meat yield increased (percentage points) in samples pretreated with condensed phosphate over respective control samples after 2, 4 and 7 day ice storage was 4.18, 4.08 and 5.46 wet wt. and 0.59, 0.65 and 1.20 dry wt., respectively (Table 1). The meat yield increased by condensed phosphate treatment was due to the functions of condensed phosphate which could retard the solubility of shrimp musculature and the loss of soluble dry matter during steam precooking.

Degradation of the shrimp musculature during ice storage enhanced water-holding capacity through steam precooking. Cooked meat moisture content increased as storage time in ice was extended. Meat yield (wet wt.) increased little between 2 and 4 day ice storage, but a tremendous loss of dry matter reduced meat yield (wet wt.) between 4 and 7 day ice storage.

The reason meat yield from control sample (23-27%) was still higher than a commercial average (20-22%) might be due

Table 1. Meat yield and moisture content of cooked shrimp meat.

| Treatment | Ice storage (days) | Wt. of ice-stored shrimp (kg) | Wt. of deiced shrimp (kg) | Meat yield | | | Moisture content (%) | |
|------------------------|----------------------|-------------------------------|---------------------------|-------------|-------------|-------------|----------------------|------------|
| | | | | Weight (gm) | Wet wt. (%) | Dry Wt. (%) | | |
| Phosphate ¹ | 2 | 11.0 | 11.000 | 3321.2 | 30.19 | 5.98 | 80.20±0.05 | |
| | | 11.0 | 11.700 | 3339.4 | 31.21 | 6.18 | | |
| | 4 | 12.0 | 11.625 | 3626.2 | 31.19 | 5.96 | 80.88±0.04 | |
| | | 12.0 | 11.600 | 3624.5 | 31.25 | 5.98 | | |
| | 7 | 13.0 | 12.300 | 3610.7 | 29.34 | 5.49 | 81.30±0.15 | |
| | | 13.0 | 12.325 | 3582.7 | 29.07 | 5.44 | | |
| | Control ² | 2 | 14.0 | 12.600 | 3363.8 | 26.70 | 5.53 | 79.30±0.04 |
| | | | 14.0 | 12.475 | 3268.6 | 26.35 | 5.45 | |
| 4 | | 15.0 | 14.225 | 3861.8 | 27.15 | 5.32 | 80.39±0.04 | |
| | | 15.0 | 14.550 | 3947.6 | 27.13 | 5.32 | | |
| 7 | | 16.0 | 15.000 | 3591.5 | 23.94 | 4.30 | 82.04±0.01 | |
| | | 15.7 | 14.650 | 3451.6 | 23.56 | 4.32 | | |

¹Pretreated with 6% condensed phosphate, 3.3°C (38°F)

²Pretreated with water, 3.3°C (38°F)

to the lower water treatment temperature (3.3°C; 38°F) employed. Apparently, cold water retarded degradative action and decreased the loss of solids before precooking.

Changes in Phosphorus, Iron and Copper Contents

The incremental increase of phosphorus content (mg P₂O₅/100 gm wet wt.) by condensed phosphate pretreatment over respective control samples after 2, 4 and 7 days of ice storage was 91.20, 134.34 and 184.68, respectively (Table 2). Added phosphorus appeared to be directly related to the degree of degradation induced by ice storage. These results confirm the findings of Nouchpramool (1979) who reported that degradation of the shrimp musculature enhanced the interaction between polyphosphate solution and shrimp musculature proteins during steam precooking. The decrease of phosphorus content observed during ice storage was due to the storage mediated loss of soluble solid material containing in situ phosphorus during steam precooking.

The higher iron and copper contents in pretreated and fresher shrimp meat are also related to the loss of soluble solid material. The metal-complexing ability of condensed phosphate may also be responsible for higher iron and copper contents in condensed phosphate pretreated meat.

Changes in Tyrosine Content

Tyrosine is liberated from proteins and peptides during the process of enzymatic proteolysis in shrimp muscle

Table 2. Mean¹ levels of phosphorus², iron³ and copper³ contents in cooked shrimp meat.

| Treatment | Ice storage (days) | P ₂ O ₅ | Fe | Cu |
|------------------------|--------------------|-------------------------------|------------|------------|
| Phosphate ⁴ | 2 | 933.74±37.62 | 17.89±0.12 | 17.30±0.39 |
| | 4 | 860.42± 8.84 | 15.62±0.49 | 13.48±0.03 |
| | 7 | 761.42±57.02 | 12.55±0.47 | 14.74±0.02 |
| Control ⁵ | 2 | 842.54±30.09 | 12.47±0.43 | 17.19±0.11 |
| | 4 | 726.08± 4.98 | 12.32±0.13 | 13.15±0.20 |
| | 7 | 577.74±23.56 | 9.95±0.12 | 13.26±0.65 |

¹n=2

²Mg P₂O₅/100 gm (wet wt.)

³ug/gm (dry wt.)

⁴Pretreated with 6% condensed phosphate, 3.3°C (38°F)

⁵Pretreated with water, 3.3°C (38°F)

(Flores and Crawford, 1973). Table 3 summarize the level of tyrosine in frozen cooked shrimp meat with respect to treatment, ice storage and frozen storage. Analysis of variance using a factorial design (Table 4) showed that variations in tyrosine level were mediated by ice storage. Apparently, there was no significant effect of frozen storage which indicate that steam precooking and frozen storage minimize enzymatic proteolysis.

During extended ice storage, tyrosine levels progressively increased in cooked shrimp meat through degradation in the round shrimp. The tremendous decrease of tyrosine levels in cooked meat at 7 days of ice storage was directly related to the marked loss of solids during steam precooking. Clearly, the condensed phosphate pretreatment maintained the physical integrity of musculature even after 7 days of ice storage. However, analysis of variance still showed that the levels of tyrosine in phosphate pretreated shrimp did not vary significantly from control samples.

Changes in TMAO Content

TMAO is a compound naturally present in many marine fish. Its physiological role is believed to be similar to the formation of urea and uric acid in land mammals; it is excreted to maintain nitrogen balance.

The extensive use of the amounts of TMA which derived from TMAO by bacterial degradation as a spoilage test of marine fish make the measurement of TMAO important. Flores

Table 3. Mean¹ levels of tyrosine (ug/gm) in frozen cooked shrimp meat

| Cooked shrimp frozen storage (months) | Round shrimp ice storage (days) | | | | | |
|---|---------------------------------|----------------------|------------------------|----------------------|------------------------|----------------------|
| | 2 | | 4 | | 7 | |
| | Phosphate ² | Control ³ | Phosphate ² | Control ³ | Phosphate ² | Control ³ |
| 0 | 239.1±18.1 | 228.8±11.3 | 261.7± 7.9 | 282.4± 6.9 | 285.4± 2.0 | 234.6±10.0 |
| 1 | 235.4± 5.1 | 242.0± 0.8 | 274.5± 3.9 | 285.6± 4.7 | 290.0± 0.6 | 250.0± 0.4 |
| 2 | 225.6± 5.1 | 242.4± 3.9 | 283.0± 2.3 | 309.4± 7.1 | 309.5± 1.1 | 270.0± 1.6 |
| 3 | 228.2±11.8 | 254.4± 1.4 | 305.0± 4.0 | 332.7± 7.9 | 321.8± 7.1 | 282.4± 1.0 |
| 4 | 245.5± 5.1 | 276.1± 4.8 | 299.4± 0.9 | 314.4± 4.1 | 309.8± 3.3 | 275.8± 5.5 |
| 5 | 251.7± 8.0 | 276.3±10.0 | 308.0± 1.0 | 326.8± 5.9 | 318.9±15.8 | 258.8± 3.0 |
| 6 | 251.6± 0.4 | 254.4± 4.9 | 303.0± 4.4 | 314.7± 4.6 | 316.8±10.7 | 264.8± 6.4 |
| 7 | 249.9± 0.6 | 269.7± 1.4 | 303.2± 3.2 | 320.2± 2.1 | 320.0± 9.4 | 279.2± 2.8 |
| 8 | 240.9± 0.5 | 254.2± 5.1 | 309.0± 0.2 | 303.8± 3.1 | 313.4± 3.0 | 259.0± 4.9 |
| 9 | 252.1± 7.7 | 235.2± 0.9 | 303.2± 0.4 | 301.8± 3.6 | 308.2±15.4 | 248.9± 3.7 |
| 10 | 234.4± 4.8 | 249.0± 1.6 | 300.4± 0.9 | 300.5± 2.9 | 309.4± 0.9 | 258.4± 2.0 |
| 11 | 227.0±10.9 | 252.6± 1.9 | 291.8±11.8 | 303.6± 3.6 | 304.6± 2.8 | 266.2± 1.0 |

¹n=2

²Pretreated with 6% condensed phosphate, 3.3°C (38°F)

³Pretreated with water, 3.3°C (38°F)

Table 4. Factorial analysis of tyrosine in frozen cooked shrimp meat

| | F-value | Ranking of level means |
|-----------------------------|-------------------|------------------------|
| Treatment (T) | 0.15 ¹ | |
| Ice storage (days) (I) | 3.50 ² | <u>4>7>2</u> |
| Frozen storage (months) (F) | 0.13 ¹ | |
| (T) X (I) | 2.42 ¹ | |
| (T) X (F) | 0.94 ¹ | |
| (I) X (F) | 0.16 ¹ | |

¹N.S. $P \leq 0.05$

²Sig. $P \geq 0.05$

Level means with the same underline did not vary significantly ($P=0.05$) from each other.

and Crawford (1973) indicated that TMAO of shrimp meat might convert to DMA and FA and possibly to TMA during ice storage.

Levels of TMAO in frozen cooked shrimp meat are listed in Table 5. Factorial analysis of variance (Table 6) showed that shrimp treated with condensed phosphate retained significantly more TMAO than respective control samples and that the amount of TMAO in cooked meat decrease progressively during ice storage. Regression analysis of TMAO levels listed in Table 5 revealed that levels decreased in an exponential manner (Table 6). Condensed phosphate pretreatment retarded the loss of moisture content and retained a higher level of water soluble TMAO through steam precooking.

The loss of TMAO content during extended ice storage was due to both microbial degradation and the washing action of melting ice. The exponential reduction of TMAO content in frozen cooked shrimp meat during storage suggested a non-enzymic reduction of TMAO. These results confirmed those of Vaisey (1956) who indicated that TMAO can be degraded by metal-complex.

Table 5. Mean¹ levels of TMAO (ug/gm) in frozen cooked shrimp meat

| Cooked shrimp frozen storage (months) | Round shrimp ice storage (days) | | | | | |
|---|---------------------------------|----------------------|------------------------|----------------------|------------------------|----------------------|
| | 2 | | 4 | | 7 | |
| | Phosphate ² | Control ³ | Phosphate ² | Control ³ | Phosphate ² | Control ³ |
| 0 | 3615± 14 | 3346± 78 | 2878± 20 | 2908± 52 | 2638± 16 | 1918± 62 |
| 1 | 3184± 81 | 3156± 50 | 2868± 04 | 2726±110 | 2071±230 | 1606± 57 |
| 2 | 2882± 47 | 3022±182 | 2738±100 | 2404± 67 | 2020± 53 | 1326± 18 |
| 3 | 2727± 85 | 2706±199 | 2482±295 | 2201± 40 | 1833± 38 | 1380±167 |
| 4 | 2698±190 | 2461±312 | 2491±151 | 2072±247 | 1936± 38 | 1265± 55 |
| 5 | 2685± 85 | 2568±112 | 2372± 42 | 2262± 27 | 1960± 50 | 1302± 14 |
| 6 | 2741± 69 | 2499± 67 | 2350±130 | 2328± 18 | 2210±110 | 1340± 40 |
| 7 | 2846± 22 | 2506±100 | 2338±144 | 2394± 20 | 2041± 26 | 1465± 48 |
| 8 | 2790± 10 | 2681±100 | 2427± 99 | 2191± 49 | 2044± 62 | 1370±161 |
| 9 | 2659± 29 | 2442± 39 | 2346± 65 | 2224±194 | 2084± 97 | 1402± 80 |
| 10 | 2585±122 | 2430±170 | 2198± 19 | 2166±195 | 1828± 39 | 1284± 32 |
| 11 | 2382±101 | 2122± 47 | 2100± 82 | 1926± 72 | 1728± 56 | 1176± 24 |

¹n = 2

²Pretreated with 6% condensed phosphate, 3.3°C (38°F)

³Pretreated with water, 3.3°C (38°F)

Table 6. Factorial and regression analyses of TMAO in frozen cooked shrimp meat.

| Factorial Analysis | | |
|-----------------------------|--------------------|---|
| | F value | Ranking of level means |
| Treatment (T) | 22.35 ⁵ | Phosphate ¹ > Control ² |
| Ice storage (days) (I) | 79.36 ⁵ | 2>4>7 |
| Frozen storage (months) (F) | 3.87 ⁵ | 0>1>2>7>8>6>3>9>5>4>10>11 |
| (T) x (I) | 4.46 ³ | |
| (T) x (F) | 11.37 ⁵ | |
| (I) x (F) | 5.68 ⁵ | |

| Regression Analysis | | | | |
|------------------------|--------------------|------------------------------|----------------------------|---------------------|
| Treatment | Ice storage (days) | Regression curve | Coefficient of correlation | F-value |
| Phosphate ¹ | 2 | $Y^6 = 3188e^{(-0.0235)X^7}$ | -0.764 | 30.92 ⁵ |
| | 4 | $Y = 2831e^{(-0.0256)X}$ | -0.804 | 40.11 ⁵ |
| | 7 | $Y = 2211e^{(-0.0164)X}$ | -0.508 | 7.65 ³ |
| Control ² | 2 | $Y = 3113e^{(-0.0301)X}$ | -0.773 | 326.40 ⁵ |
| | 4 | $Y = 2618e^{(-0.0235)X}$ | -0.670 | 17.95 ⁵ |
| | 7 | $Y = 1576e^{(-0.0229)X}$ | -0.588 | 11.63 ⁴ |

¹Pretreated with 6% condensed phosphate, 3.3°C (38°F)

²Pretreated with water, 3.3°C (38°F)

³Sig. $P \geq 0.025$

⁴Sig. $P \geq 0.005$

⁵Sig. $P \geq 0.001$

⁶Y: TMAO levels (ug/gm) in frozen cooked shrimp meat

⁷X: Frozen storage

Level means with the same underline did not vary significantly ($P=0.05$) from each other.

Changes in TMA Content

TMA has been proposed as a microbial product; its level has been linked to the action of bacterial enzymes and the numbers of bacteria in shrimp meat (Fieger and Friloux, 1954; Bailey et al., 1956; Iyenger et al., 1960). Table 7 lists TMA contents determined in cooked shrimp meat. Factorial analysis of variance (Table 8) indicates that TMA levels varied significantly by treatment, ice storage time and frozen storage time; all two-way comparisons yielded significant interactions. Condensed phosphate pretreated shrimp yielded cooked meat containing significantly less TMA than respective control samples. The levels of TMA increased during ice storage, and the amounts of TMA in cooked meat were slowly reduced during extended frozen storage. Regression analysis of levels listed in Table 8 showed that the TMA content in cooked shrimp meat possessed an exponential relation with frozen storage time.

The inhibition of bacterial growth in round shrimp prior to processing by the condensed phosphate pretreatment may have resulted in a lower TMA content in cooked meat over controlled samples. Apparently, the microorganisms are able to grow at 2-3°C, so the TMA content increased progressively as ice storage was extended.

The application of steam precooking (101°C, 90 sec.) and freezing temperature minimized bacterial and enzymic action. The slow change of TMA during frozen storage

suggested a non-enzymic degradation. These results are supported by Vaisey (1956) who showed that TMA could be continuously degraded to DMA by non-enzymic catalysis.

Table 7. Mean¹ levels of TMA (ug/gm) in frozen cooked shrimp meat

| Cooked shrimp frozen storage (months) | Round shrimp ice storage (days) | | | | | |
|---|---------------------------------|----------------------|------------------------|----------------------|------------------------|----------------------|
| | 2 | | 4 | | 7 | |
| | Phosphate ² | Control ³ | Phosphate ² | Control ³ | Phosphate ² | Control ³ |
| 0 | 23.2±1.7 | 31.2±1.0 | 29.3±2.8 | 37.1±1.1 | 35.0±4.0 | 41.4±0.8 |
| 1 | 23.8±1.0 | 25.3±0.5 | 27.4±0.5 | 29.4±0.5 | 29.1±0.5 | 31.9±1.0 |
| 2 | 20.7±1.0 | 22.9±0.2 | 23.6±1.9 | 27.2±0.5 | 28.0±1.8 | 29.0±0.5 |
| 3 | 20.0±1.2 | 21.1±0.2 | 23.8±0.2 | 24.3±0.7 | 27.7±0.5 | 26.9±0.9 |
| 4 | 17.3±3.3 | 22.6±1.9 | 23.6±0.5 | 25.2±1.2 | 26.6±0.6 | 26.3±0.5 |
| 5 | 17.7±2.2 | 22.6±1.6 | 21.0±1.1 | 23.0±0.9 | 27.5±0.1 | 26.5±1.1 |
| 6 | 17.7±1.2 | 23.7±0.5 | 19.9±1.1 | 24.0±0.8 | 25.9±0.5 | 28.5±0.4 |
| 7 | 14.7±1.4 | 20.9±1.0 | 18.6±0.9 | 22.1±1.8 | 22.7±1.3 | 25.8±0.6 |
| 8 | 16.2±1.3 | 19.9±0.9 | 18.4±0.4 | 20.9±0.1 | 21.0±0.2 | 23.4±1.3 |
| 9 | 16.2±1.3 | 17.9±0.9 | 18.3±0.7 | 21.6±0.6 | 21.5±0.4 | 22.6±0.6 |
| 10 | 14.8±0.8 | 16.7±1.5 | 18.0±1.1 | 21.1±0.3 | 19.1±0.2 | 22.2±0.2 |
| 11 | 13.0±0.2 | 14.7±0.4 | 16.8±0.5 | 18.8±0.4 | 19.7±0.5 | 21.4±0.4 |

¹n = 2

²Pretreated with 6% condensed phosphate, 3.3°C (38°F)

³Pretreated with water, 3.3°C (38°F)

Table 8. Factorial and regression analyses of TMA in frozen cooked shrimp meat.

| Factorial Analysis | | | | |
|-----------------------------|--|---------------------|---|--|
| | | F value | Ranking of level means | |
| Treatment (T) | | 103.88 ³ | Control ² > Phosphate ¹ | |
| Ice storage (days) (I) | | 176.86 ³ | 7 > 4 > 2 | |
| Frozen storage (months) (F) | | 77.74 ³ | 0 > 1 > 2 > 3 > 4 > 6 > 5 > 7 > 8 > 9 > 10 > 11 | |
| (T) X (I) | | 471.73 ³ | | |
| (T) X (F) | | 40.19 ³ | | |
| (I) X (F) | | 8.74 ³ | | |

| Regression Analysis | | | | |
|------------------------|--------------------|------------------------------|----------------------------|---------------------|
| Treatment | Ice storage (days) | Regression curve | Coefficient of correlation | F value |
| Phosphate ¹ | 2 | $Y^4 = 23.0e^{(-0.0481)X^5}$ | -0.841 | 53.11 ³ |
| | 4 | $Y = 27.5e^{(-0.0472)X}$ | -0.917 | 116.27 ³ |
| | 7 | $Y = 32.5e^{(-0.0482)X}$ | -0.924 | 127.70 ³ |
| Control ² | 2 | $Y = 28.0e^{(-0.0499)X}$ | -0.875 | 71.87 ³ |
| | 4 | $Y = 31.2e^{(-0.0462)X}$ | -0.895 | 88.57 ³ |
| | 7 | $Y = 34.2e^{(-0.0450)X}$ | -0.884 | 79.07 ³ |

¹Pretreated with 6% condensed phosphate, 3.3°C (38°F)

²Pretreated with water, 3.3°C (38°F)

³Sig. $P \geq 0.001$

⁴Y: TMA levels (ug/gm) in frozen cooked shrimp meat

⁵X: Frozen storage (months)

Level means with the same underline did not vary significantly ($P=0.05$) from each other

Changes in DMA Content

The formation of DMA in seafoods concerns food scientists because of the co-production of FA which may play a role in textural alterations (Tokunaga, 1956; Castell et al., 1970). Both enzymic and non-enzymic mechanisms had been proposed for the formation of DMA in seafoods (Amano and Yamada, 1965; Spinelli and Koury, 1979).

Levels of DMA in frozen cooked shrimp meat are summarized in Table 9. According to factorial analysis of variance data (Table 10) phosphate pretreated shrimp possessed a significantly higher DMA content than respective control samples and the increases in DMA were positively proportional to extended ice and frozen storage. The exponential relationship between DMA content in cooked meat and frozen storage time with respect to treatment and ice storage are listed in Table 10.

Levels of DMA in shrimp, which increased steadily throughout ice storage, were retained in cooked meat more effectively by phosphate pretreatment. DMA production during extended frozen storage suggested a non-enzymatic mechanism. Steam precooking would markedly minimize the potential for an enzymatic mechanism. These results strongly supported Spinelli and Koury (1980) who pointed out that the formation of DMA in frozen fish could take place by pathways not requiring the presence of TMAO-splitting enzymes. The heat-stable copper containing hemocyanin in shrimp body fluid

Table 9. Mean¹ levels of DMA (ug/gm) in frozen cooked shrimpmeat.

| Cooked shrimp frozen storage (months) | Round shrimp ice storage (days) | | | | | |
|---|---------------------------------|----------------------|------------------------|----------------------|------------------------|----------------------|
| | 2 | | 4 | | 7 | |
| | Phosphate ² | Control ³ | Phosphate ² | Control ³ | Phosphate ² | Control ³ |
| 0 | 5.30±0.10 | 5.13±0.07 | 5.58±0.02 | 5.36±0.06 | 6.40±0.10 | 6.26±0.04 |
| 1 | 5.36±0.06 | 5.38±0.01 | 5.54±0.14 | 5.50±0.10 | 6.71±0.09 | 5.93±0.13 |
| 2 | 5.34±0.09 | 5.05±0.17 | 5.88±0.33 | 5.46±0.08 | 6.87±0.77 | 6.29±0.07 |
| 3 | 5.27±0.03 | 5.20±0.18 | 5.66±0.10 | 5.30±0.08 | 6.88±0.02 | 6.04±0.02 |
| 4 | 5.42±0.12 | 5.44±0.06 | 5.92±0.12 | 5.68±0.04 | 6.70±0.10 | 6.52±0.21 |
| 5 | 5.70±0.10 | 5.53±0.07 | 6.21±0.09 | 5.92±0.15 | 6.78±0.08 | 6.62±0.08 |
| 6 | 5.88±0.17 | 5.59±0.18 | 6.32±0.24 | 5.82±0.10 | 7.08±0.08 | 6.55±0.05 |
| 7 | 6.15±0.07 | 5.96±0.12 | 6.46±0.23 | 6.03±0.07 | 7.36±0.27 | 6.93±0.08 |
| 8 | 6.85±0.05 | 6.30±0.10 | 6.75±0.25 | 6.60±0.20 | 8.10±0.30 | 7.35±0.25 |
| 9 | 7.03±0.04 | 6.85±0.05 | 7.59±0.04 | 7.00±0.11 | 8.58±0.06 | 7.60±0.10 |
| 10 | 7.48±0.04 | 7.15±0.14 | 8.37±0.05 | 7.50±0.11 | 8.88±0.08 | 8.01±0.08 |
| 11 | 8.30±0.02 | 7.34±0.04 | 8.45±0.05 | 7.62±0.12 | 8.95±0.05 | 8.17±0.01 |

¹n = 2

²Pretreated with 6% condensed phosphate, 3.3°C (38°F)

³Pretreated with water, 3.3°C (38°F)

Table 10. Factorial and regression analyses of DMA in frozen cooked shrimp meat.

| Factorial Analysis | | | | |
|-----------------------------|--|----------------------|---|--|
| | | F value | Ranking of level means | |
| Treatment (T) | | 142.32 ³ | Phosphate ¹ > Control ² | |
| Ice storage (days) (I) | | 352.75 ³ | 7 > 4 > 2 | |
| Frozen storage (months) (F) | | 212.06 ³ | 11 > 10 > 9 > 8 > 7 > 6 > 5 > 4 > 2 > 3 > 1 > 0 | |
| (T) X (I) | | 1212.72 ³ | | |
| (T) X (F) | | 72.62 ³ | | |
| (I) X (F) | | 10.79 ³ | | |

| Regression Analysis | | | | |
|------------------------|--------------------|-----------------------------|----------------------------|---------------------|
| Treatment | Ice storage (days) | Regression curve | Coefficient of correlation | F value |
| Phosphate ¹ | 2 | $Y^4 = 4.86e^{(0.0412)X^5}$ | 0.939 | 164.00 ³ |
| | 4 | $Y = 5.26e^{(0.0383)X}$ | 0.917 | 116.27 ³ |
| | 7 | $Y = 6.23e^{(0.0308)X}$ | 0.917 | 116.27 ³ |
| Control ² | 2 | $Y = 4.84e^{(0.0348)X}$ | 0.932 | 145.46 ³ |
| | 4 | $Y = 5.07e^{(0.0337)X}$ | 0.929 | 138.63 ³ |
| | 7 | $Y = 5.83e^{(0.0283)X}$ | 0.932 | 145.46 ³ |

¹Pretreated with 6% condensed phosphate, 3.3°C (38°F)

²Pretreated with water, 3.3°C (38°F)

³Sig. $P \geq 0.001$

⁴Y: DMA levels (ug/gm) in frozen cooked shrimp meat

⁵X: Frozen storage

Level means with the same underline did not vary significantly ($P=0.05$) from each other

could be the factor which catalyzed the DMA forming reaction after cooking. The higher slope functions obtained by regression analysis of the DMA levels in phosphate treated and fresher shrimp might be due to higher body fluid content retained through steam precooking. This observation is supported by the higher iron and copper levels contained in phosphate treated and fresher shrimp (Table 2).

Changes in Levels of Objective Texture Measurement

The textural deterioration of fish usually happens in frozen storage. Sometimes toughening of fish muscle occurs more quickly at low storage temperature. Toughening is related to protein denaturation. The progressive formation of FA during frozen storage has been suggested to be a major factor mediating the denaturation of shrimp muscle proteins.

The values for samples of cooked shrimp meat of total work and maximum force measured by Allo-Kramer shear press are summarized in Table 11. Factorial analysis of variance (Table 12) showed that treatment, ice storage and frozen storage varied values for total work and maximum force in a significant manner. Regression analysis (Table 13) showed a linear relationship between both objective texture measurements and frozen storage time.

Toughness measured by shear press was highly related to the condensed phosphate pretreatment. The polyphosphate solution interacted with collagen-like proteins to form a

Table 11. Mean¹ levels of objective texture measurements of frozen cooked shrimp meat².

| | | Total work (inch-pounds) | | | | |
|------------------------|--------------------|----------------------------|--------------|--------------|--------------|--------------|
| Treatment | Ice storage (days) | Frozen storage (months) | | | | |
| | | 0 | 3 | 6 | 9 | 11 |
| Phosphate ³ | 2 | 117.67± 1.53 | 128.00± 1.73 | 132.67± 2.00 | 143.67± 3.21 | 136.00± 3.00 |
| | 4 | 090.00± 4.36 | 84.67± 5.13 | 86.00± 3.00 | 102.33± 5.03 | 106.00± 8.89 |
| | 7 | 103.33± 4.16 | 96.67± 2.00 | 88.67± 4.16 | 109.33± 4.93 | 117.00±10.44 |
| Control ⁴ | 2 | 141.00± 2.64 | 154.00± 9.54 | 129.67± 3.51 | 169.00±12.53 | 174.00± 6.93 |
| | 4 | 109.00± 2.64 | 103.67± 8.50 | 97.67± 2.52 | 131.67± 5.51 | 125.33± 4.72 |
| | 7 | 125.33±10.50 | 100.00± 3.00 | 104.00± 2.00 | 121.33± 2.31 | 131.00± 7.81 |

| | | Maximum force (pounds) | | | | |
|------------------------|--------------------|--------------------------|--------------|--------------|--------------|--------------|
| Treatment | Ice storage (days) | Frozen sotrage (months) | | | | |
| | | 0 | 3 | 6 | 9 | 11 |
| Phosphate ³ | 2 | 198.33± 9.07 | 239.00± 7.55 | 237.33± 6.43 | 274.33± 6.43 | 257.00±14.73 |
| | 4 | 160.00± 5.00 | 150.00± 7.00 | 153.00± 2.65 | 181.33±18.04 | 191.33±12.10 |
| | 7 | 162.67± 5.51 | 176.33± 3.06 | 164.33± 4.04 | 189.00±10.82 | 210.33±12.53 |
| Control ⁴ | 2 | 270.00± 4.58 | 315.00±47.84 | 240.00± 5.00 | 364.33±27.23 | 325.67± 7.50 |
| | 4 | 190.67± 8.50 | 191.67± 5.51 | 172.00±11.13 | 266.67±24.66 | 226.67± 4.04 |
| | 7 | 223.67±17.24 | 200.67± 2.31 | 190.00± 2.00 | 242.67±13.65 | 229.67±10.41 |

¹n = 3

²All samples on 150 gm drained weight basis

³Pretreated with 6% condensed phosphate, 3.3°C (38°F)

⁴Pretreated with water, 3.3°C (38°F)

Table 12. Factorial analyses of objective texture measurements of cooked shrimp meat.

| Total Work (inch-pounds) | | |
|-----------------------------|---------------------|---|
| | F value | Ranking of level means |
| Treatment (T) | 224.46 ¹ | Control ³ > Phosphate ² |
| Ice storage (days) (I) | 783.87 ¹ | 2 > 7 > 4 |
| Frozen storage (months) (F) | 69.14 ¹ | <u>11</u> > 9 > 0 > 3 > 6 |
| (T) X (I) | 191.79 ¹ | |
| (T) X (F) | 223.76 ¹ | |
| (I) X (F) | 41.95 ¹ | |

| Maximum Force (pounds) | | |
|-----------------------------|---------------------|---|
| | F value | Ranking of level means |
| Treatment (T) | 250.95 ¹ | Control ³ > Phosphate ² |
| Ice storage (days) (I) | 320.47 ¹ | 2 > 7 > 4 |
| Frozen storage (months) (F) | 61.14 ¹ | 9 > 11 > 3 > 0 > 6 |
| (T) X (I) | 182.19 ¹ | |
| (T) X (F) | 190.80 ¹ | |
| (I) X (F) | 46.65 ¹ | |

¹Sig. $P \geq 0.001$

²Pretreated with 6% condensed phosphate, 3.3°C (38°F)

³Pretreated with water, 3.3°C (38°F)

Level means with the same underline did not vary significantly ($P=0.05$) from each other

Table 13. Regression the values of objective texture measurement on frozen storage

| Treatment | Ice | (Total work) ³ | R value | F value |
|------------------------------|-------------------|---------------------------|---------|--------------------|
| | storage (days) | Regression equation | | |
| phosphate ¹ | 2 | Y=120.37+1.94X | 0.864 | 38.27 ⁹ |
| | 4 | Y= 83.73+1.74X | 0.699 | 12.42 ⁸ |
| | 7 | Y= 95.20+1.34X | 0.489 | 4.08 ⁶ |
| Control ² | 2 | Y=137.15+2.82X | 0.628 | 7.80 ⁷ |
| | 4 | Y=100.94+2.16X | 0.628 | 8.48 ⁷ |
| | 7 | Y=110.20+1.06X | 0.319 | 1.47 ⁵ |
| (Maximum force) ⁴ | | | | |
| phosphate ¹ | 2 | Y=208.65+5.61X | 0.844 | 32.28 ⁹ |
| | 4 | Y=148.16+3.27X | 0.704 | 12.80 ⁸ |
| | 7 | Y=158.94+3.71X | 0.785 | 20.94 ⁹ |
| control ² | 2 | Y=269.19+5.83X | 0.481 | 3.91 ⁶ |
| | 4 | Y=179.07+5.12X | 0.582 | 6.67 ⁷ |
| | 7 | Y=206.32+1.90X | 0.355 | 1.87 ⁵ |

¹ Pretreated with 6% condensed phosphate, 3.3°C (38°F)

² Pretreated with water, 3.3°C (38°F)

³ Y: total work (inch-pound); X: frozen storage (months)

⁴ Y: maximum force (pound); X: frozen storage (months)

⁵ N.S. $P \leq 0.05$

⁶ Sig. $P \geq 0.10$

⁷ Sig. $P \geq 0.025$

⁸ Sig. $P \geq 0.005$

⁹ sig. $P \geq 0.001$

gelatinized complex on the surface of shrimp meat during steam precooking. The gelatinized complex retarded the loss of body fluid and solids yielding cooked meat containing a higher moisture content associated with less solids of a different overall composition. This alteration produced less resistance to compression by the shear press.

Deterioration of shrimp muscle during ice storage enhanced cooked meat moisture, DMA and FA contents. DMA and FA formation in cooked meat was catalyzed by a non-enzymic system during frozen storage. Apparently, the capability of retaining the factor required for catalyzing formation varied by treatment and ice storage time. Phosphate treated and fresher shrimp formed DMA and presumably FA more rapidly during extended frozen storage. The texture of frozen cooked shrimp meat was simultaneously influenced by those factors which were responsible for the unordered ranking of both texture measurements with respect to ice storage and frozen storage.

Regression of DMA levels observed during frozen storage on shear values for total work correlated in a linear manner (Table 14). These results supported the potential influence of FA on meat texture by mediating denaturation of its muscle proteins. The mechanism by which FA affects proteins at the molecular level was postulated from the fact that FA has the ability to bind covalently to various functional groups in the protein and cause a deformation accompanied by

Table 14. Regression analysis of total work on DMA content

| Treatment | Ice storage (days) | Regression equation ³ | R value | F value |
|------------------------|--------------------|----------------------------------|---------|--------------------|
| phosphate ¹ | 2 | $Y=98.23+ 5.25X$ | 0.704 | 12.81 ⁶ |
| | 4 | $Y=50.98+ 6.25X$ | 0.836 | 30.18 ⁷ |
| | 7 | $Y=47.45+ 7.33X$ | 0.672 | 10.70 ⁵ |
| control ² | 2 | $Y=63.68+14.92X$ | 0.755 | 17.20 ⁶ |
| | 4 | $Y=41.40+11.59X$ | 0.789 | 21.48 ⁷ |
| | 7 | $Y=67.81+ 6.40x$ | 0.487 | 4.04 ⁴ |

¹Pretreated with 6% condensed phosphate, 3.3°C (38°F)

²Pretreated with water, 3.3°C (38°F)

³Y: total work (inch-pound); X: DMA content (ug/g)

⁴Sig. $P \geq 0.10$

⁵Sig. $P \geq 0.01$

⁶Sig. $P \geq 0.005$

⁷Sig. $P \geq 0.001$

cross-linking between the protein peptide chains via methylene bridges (Walker, 1964).

Sensory Evaluation of Quality frozen Cooked Shrimp Meat

Flavor panels were employed to evaluate the effect of treatment, ice storage and frozen storage on the cooked shrimp meat quality. Mean scores and factorial analyses of variance for color, texture, juiciness, flavor and overall desirability are summarized in Table 15 through 19, respectively, and illustrated on Figure 2 through 11.

Analyses of variance showed that treatment, ice storage and frozen storage had significant interactions with each other in all sensory evaluations. The scores of pretreated shrimp meat for all sensory factors were superior to respective control samples.

Ranking of level means showed that flavor panel scores varied significantly with ice storage. They also indicated that 7 day old shrimp were inferior to 2 and 4 day old shrimp in all cases. Color and texture scores from 2 day old shrimp were superior to that from 4 day old shrimp. But juiciness, flavor and overall desirability scores from 2 day old shrimp were inferior to 4 day old shrimp.

Frozen storage did not significantly affect scores for texture and juiciness. Ranking of level means also showed color, flavor and overall desirability scores varied significantly, but the variation did not change in an ordered

manner with respect to time.

Condensed phosphate treatment retarded the loss of body fluid and solids during precooking and reduced the chemical degradation during precooking and frozen storage. These actions produced alterations in cooked meat that were preferred over control samples by judges.

The overall quality revealed by analysis of variance reflected a significant deterioration in 7 day old shrimp. Scores for 2 and 4 day old shrimp varied little. Degradation of round shrimp during ice storage certainly contributed to instability during frozen storage which might have played an important role in mediation of the results observed.

During extended storage, and increased toughness in shrimp meat was reflected in the objective texture measurement. Sensory texture scores did not significantly change with respect to storage time. Texture deterioration, while reflected in objective tests, was not extensive enough for detection by sensory procedures. Mixing of meat with saliva and the presence of natural fats and juices influenced sensory perception of texture.

No significant changes in juiciness scores could be attributed to the quick freezing rate, stable storage temperature and moisture-proof film seal which retard the formation and accretion of ice crystals and prevented the dehydration of shrimp meat during extended frozen storage.

The initial difference of sensory quality and the different degradation rate during frozen storage were responsible for the unordered changes in color, flavor and overall desirability scores. Especially, since sensory evaluations were carried out at different times making it difficult for judges to relate quantitatively sensory scores to storage time.

Table 15. Mean³ color scores for frozen cooked shrimp meat

| Treatment | Ice storage (days) | Frozen storage (days) | | | | | Total mean ⁴ of treatment | Total mean ⁵ of ice storage |
|---|--------------------|-----------------------|------|------|------|------|--------------------------------------|--|
| | | 11 | 107 | 200 | 283 | 330 | | |
| Phosphate ¹ | 2 | 7.90 | 7.55 | 7.55 | 7.50 | 7.50 | 7.22 | 7.51 (2 day) |
| | 4 | 7.45 | 6.90 | 7.05 | 7.35 | 7.45 | | |
| | 7 | 6.80 | 6.55 | 6.75 | 6.80 | 7.20 | | |
| Control ² | 2 | 7.60 | 7.15 | 7.05 | 7.65 | 7.65 | 6.89 | 7.15 (4 day) |
| | 4 | 7.40 | 6.90 | 6.80 | 6.85 | 7.35 | | |
| | 7 | 5.85 | 5.70 | 6.10 | 6.50 | 6.85 | | |
| Total mean ⁶ of frozen storage | | 7.17 | 6.79 | 6.88 | 7.11 | 7.33 | | |

Factorial Analysis

| | F value | Ranking of level means |
|--------------------|--------------------|---|
| Treatment (T) | 10.06 ⁸ | phosphate ¹ > control ² |
| Ice storage (I) | 32.09 ⁹ | 2 > 4 > 7 |
| Frozen storage (F) | 3.61 ⁷ | 330 > <u>11</u> > <u>283</u> > 200 > 107 |
| (T) X (I) | 15.68 ⁸ | |
| (T) X (F) | 20.36 ⁸ | |
| (I) X (F) | 3.37 ⁹ | |

¹ Pretreated with 6% condensed phosphate

² Pretreated with water

³ n = 30

⁴ n = 300

⁵ n = 200

⁶ n = 120

⁷ Sig. P ≥ 0.01

⁸ Sig. P ≥ 0.005

⁹ Sig. P ≥ 0.001

Level means with the same underline did not vary significantly (P=0.05) for each other from each other

Table 16. Mean³ texture scores for frozen cooked shrimp meat

| Treatment | Ice Storage (days) | Frozen storage (days) | | | | | Total mean ⁴ of treatment | Total mean ⁵ of ice storage |
|---|--------------------|-----------------------|------|------|------|------|--------------------------------------|--|
| | | 11 | 107 | 200 | 283 | 330 | | |
| Phosphate ¹ | 2 | 7.35 | 6.95 | 6.95 | 6.90 | 6.90 | 6.80 | 6.90 (2 day) |
| | 4 | 7.25 | 6.90 | 6.75 | 6.90 | 7.05 | | |
| | 7 | 6.25 | 6.25 | 6.60 | 6.50 | 6.50 | | |
| Control ² | 2 | 7.45 | 6.90 | 6.30 | 6.55 | 6.70 | 6.57 | 6.81 (4 day) |
| | 4 | 6.95 | 6.10 | 6.70 | 6.55 | 6.95 | | |
| | 7 | 6.10 | 6.20 | 6.20 | 6.40 | 6.50 | | |
| Total mean ⁶ of frozen storage | | 6.89 | 6.55 | 6.58 | 6.40 | 6.77 | | |

Factorial analysis

| | F value | Ranking of level means |
|--------------------|---------------------|---|
| Treatment (T) | 4.54 ⁸ | phosphate ¹ > control ² |
| Ice sotrage (I) | 9.85 ¹⁰ | 2 > 4 > 7 |
| Frozen storage (F) | 1.39 ⁷ | |
| (T) X (I) | 10.25 ¹⁰ | |
| (T) X (F) | 8.66 ¹⁰ | |
| (I) X (F) | 2.44 ⁹ | |

¹Pretreated with 6% condensed phosphate

²Pretreated with water

³n = 30

⁴n = 300

⁵n = 200

⁶n = 120

⁷N. S. P ≤ 0.05

⁸Sig. P ≥ 0.05

⁹Sig. P ≥ 0.025

¹⁰Sig. P ≥ 0.001

Level means with the same underline did not vary significantly (P=0.05) from each other

Table 17. Mean³ juiciness scores for frozen cooked shrimp meat

| Treatment | Ice storage (days) | Frozen storage (days) | | | | | Total mean ⁴ of treatment | Total mean ⁵ of ice storage |
|---|--------------------|-----------------------|------|------|------|------|--------------------------------------|--|
| | | 11 | 107 | 200 | 283 | 330 | | |
| Phosphate ¹ | 2 | 7.10 | 6.85 | 6.80 | 6.75 | 6.95 | 6.90 | 6.78 (2 day) |
| | 4 | 7.00 | 7.05 | 6.95 | 7.00 | 7.30 | | |
| | 7 | 6.85 | 6.90 | 6.95 | 6.40 | 6.60 | | |
| Control ² | 2 | 7.25 | 6.35 | 6.55 | 6.50 | 6.65 | 6.55 | 6.90 (4 day) |
| | 4 | 6.75 | 6.60 | 6.95 | 6.45 | 6.95 | | |
| | 7 | 6.30 | 6.30 | 6.25 | 6.25 | 6.45 | | |
| Total mean ⁶ of frozen storage | | 6.88 | 6.67 | 6.74 | 6.56 | 6.82 | | |

Factorial Analysis

| | F value | Ranking of level means |
|--------------------|--------------------|---|
| Treatment (T) | 9.15 ⁸ | phosphate ¹ > control ² |
| Ice storage (I) | 4.15 ⁹ | 4 > 2 > 7 |
| Frozen storage (F) | 1.05 ⁷ | |
| (T) X (I) | 6.42 ¹⁰ | |
| (T) X (F) | 4.25 ¹⁰ | |
| (I) X (F) | 2.22 ⁸ | |

¹Pretreated with 6% condensed phosphate

²Pretreated with water

³n = 30

⁴n = 300

⁵n = 200

⁶n = 120

⁷N. S. P ≤ 0.05

⁸Sig. P ≥ 0.05

⁹Sig. P ≥ 0.025

¹⁰Sig. P ≥ 0.005

Level means with the same underline did not vary significantly (P=0.05) from each other

Table 18. Mean³ flavor scores for frozen cooked shrimp meat

| Treatment | Ice storage (days) | Frozen storage (days) | | | | | Total mean ⁴ of treatment | Total mean ⁵ of ice storage |
|---|--------------------|-----------------------|------|------|------|------|--------------------------------------|--|
| | | 11 | 107 | 200 | 283 | 330 | | |
| Phosphate ¹ | 2 | 7.15 | 6.85 | 7.20 | 6.30 | 6.70 | 6.64 | 6.68 (2 say) |
| | 4 | 7.20 | 6.75 | 7.15 | 6.80 | 6.85 | | |
| | 7 | 6.20 | 6.40 | 6.60 | 5.40 | 6.10 | | |
| Control ² | 2 | 7.30 | 6.90 | 6.40 | 5.85 | 6.15 | 6.28 | 6.78 (4 day) |
| | 4 | 6.80 | 6.30 | 6.70 | 6.55 | 6.75 | | |
| | 7 | 5.50 | 5.75 | 5.80 | 5.60 | 5.90 | | 5.92 (7 day) |
| Total mean ⁶ of frozen storage | | 6.69 | 6.49 | 6.64 | 6.08 | 6.41 | | |

Factorial Analysis

| | F value | Ranking fo levelmeans |
|--------------------|---------------------|---|
| Treatment (T) | 7.77 ⁹ | phosphate ¹ > control ² |
| Ice storage (I) | 17.59 ¹⁰ | 4 > 2 > 7 |
| Frozen storage (F) | 2.78 ⁷ | 11 > 200 > 107 > 330 > 283 |
| (T) X (I) | 12.70 ¹⁰ | |
| (T) X (F) | 12.36 ¹⁰ | |
| (I) X (F) | 2.76 ⁸ | |

¹ Pretreated with 6% condensed phosphate

² Pretreated with water

³ n = 30

⁴ n = 300

⁵ n = 200

⁶ n = 120

⁷ Sig. P ≥ 0.05

⁸ Sig. P ≥ 0.025

⁹ Sig. P ≥ 0.01

¹⁰ Sig. P ≥ 0.001

Level means with the same underline did not vary significantly (P=0.05) from each other

Table 19. Mean³ overall desirability scores for frozen cooked shrimp meat

| Treatment | Ice storage (days) | Frozen storage (days) | | | | | Total mean ⁴ of treatment | Total mean ⁵ of ice storage |
|---|--------------------|-----------------------|------|------|------|------|--------------------------------------|--|
| | | 11 | 107 | 200 | 283 | 330 | | |
| Phosphate ¹ | 2 | 7.15 | 6.85 | 7.05 | 6.20 | 6.70 | 6.65 | 6.62 (2 day) |
| | 4 | 7.05 | 6.75 | 7.20 | 6.80 | 6.80 | | |
| | 7 | 6.25 | 6.35 | 6.75 | 5.60 | 6.25 | | |
| Control ² | 2 | 7.10 | 6.75 | 6.50 | 5.90 | 5.95 | 6.28 | 6.77 (4 day) |
| | 4 | 6.85 | 6.25 | 6.80 | 6.40 | 6.80 | | |
| | 7 | 5.50 | 5.75 | 5.85 | 5.80 | 5.95 | | |
| Total mean ⁶ of frozen storage | | 6.65 | 6.45 | 6.69 | 6.12 | 6.41 | | |

Factorial Analysis

| | F value | Ranking of level means |
|--------------------|--------------------|---|
| Treatment (T) | 8.72 ⁸ | phosphate ¹ > control ² |
| Ice storage (I) | 14.67 ⁹ | 4 > 2 > 7 |
| Frozen storage (F) | 2.83 ⁷ | 200 > 11 > 107 > 330 > 283 |
| (T) X (I) | 13.40 ⁹ | |
| (T) X (F) | 11.20 ⁹ | |
| (I) X (F) | 3.20 ⁸ | |

¹ Pretreated with 6% condensed phosphate

² Pretreated with water

³ n = 30

⁴ n = 300

⁵ n = 200

⁶ n = 120

⁷ Sig. P ≥ 0.05

⁸ Sig. P ≥ 0.005

⁹ Sig. P ≥ 0.001

Level means with the same underline did not vary significantly (P=0.05) from each other

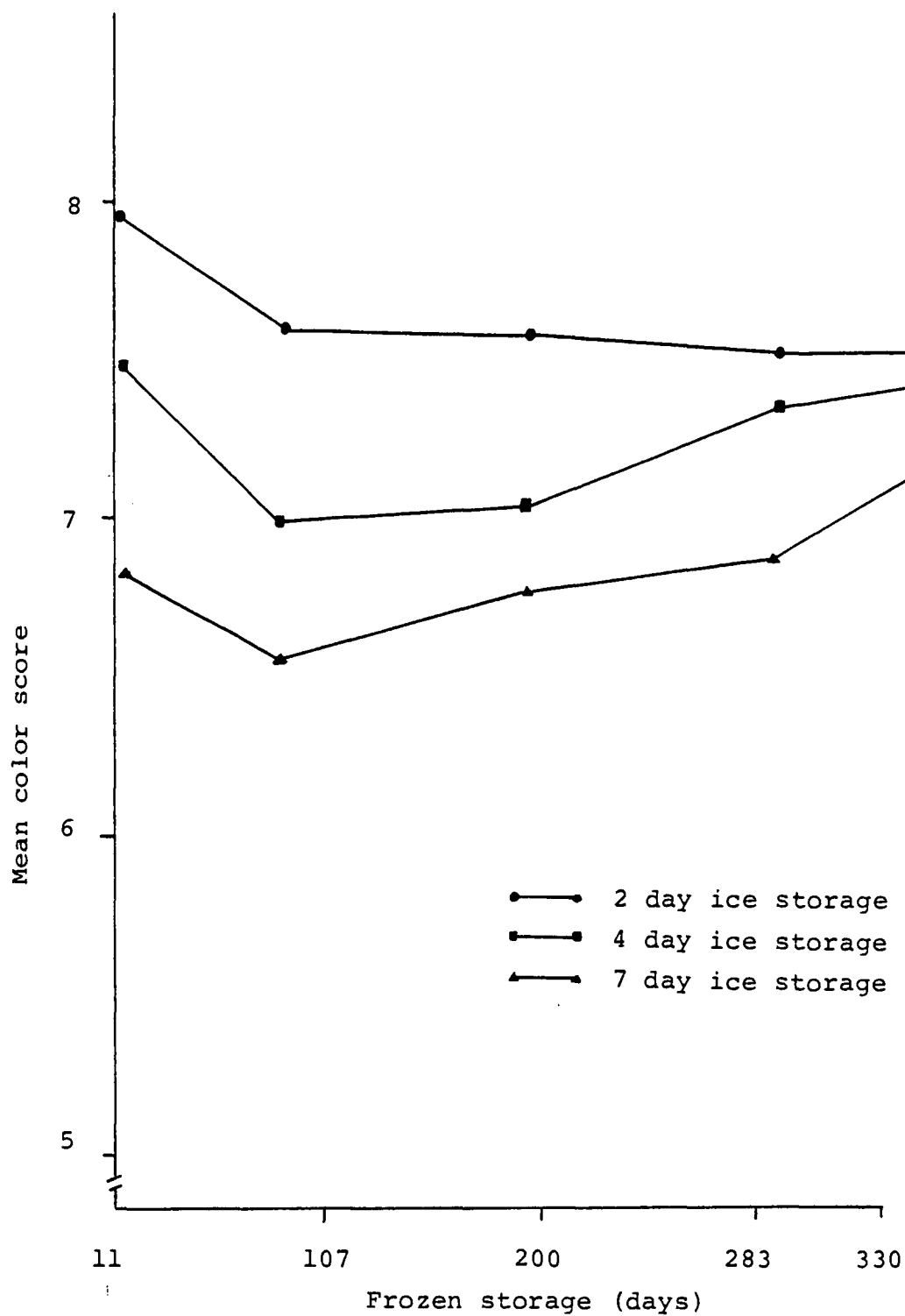


Figure 2. Mean color scores of frozen cooked shrimp meat (condensed phosphate pretreatment)

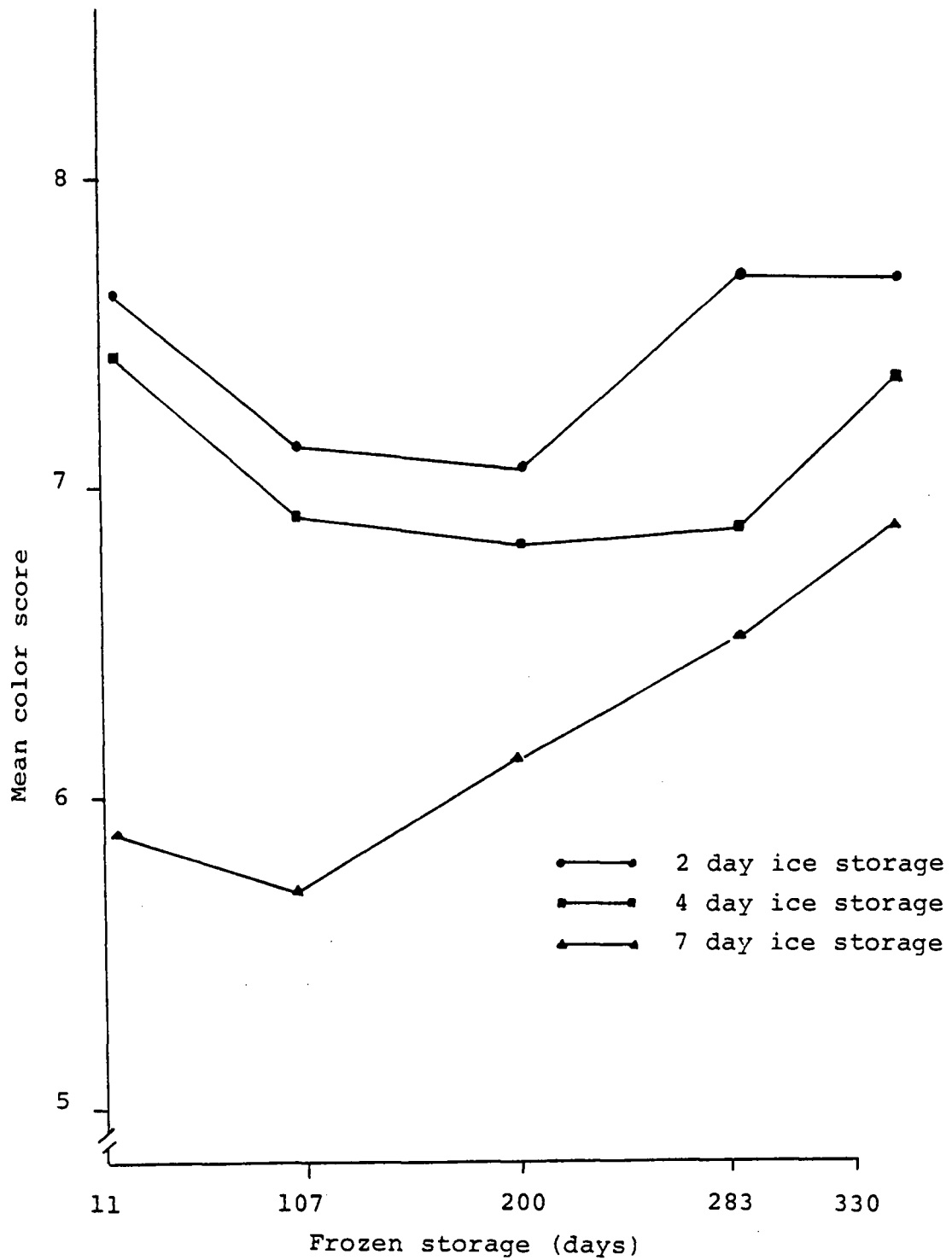


Figure 3. Mean color scores of frozen cooked shrimp meat (control)

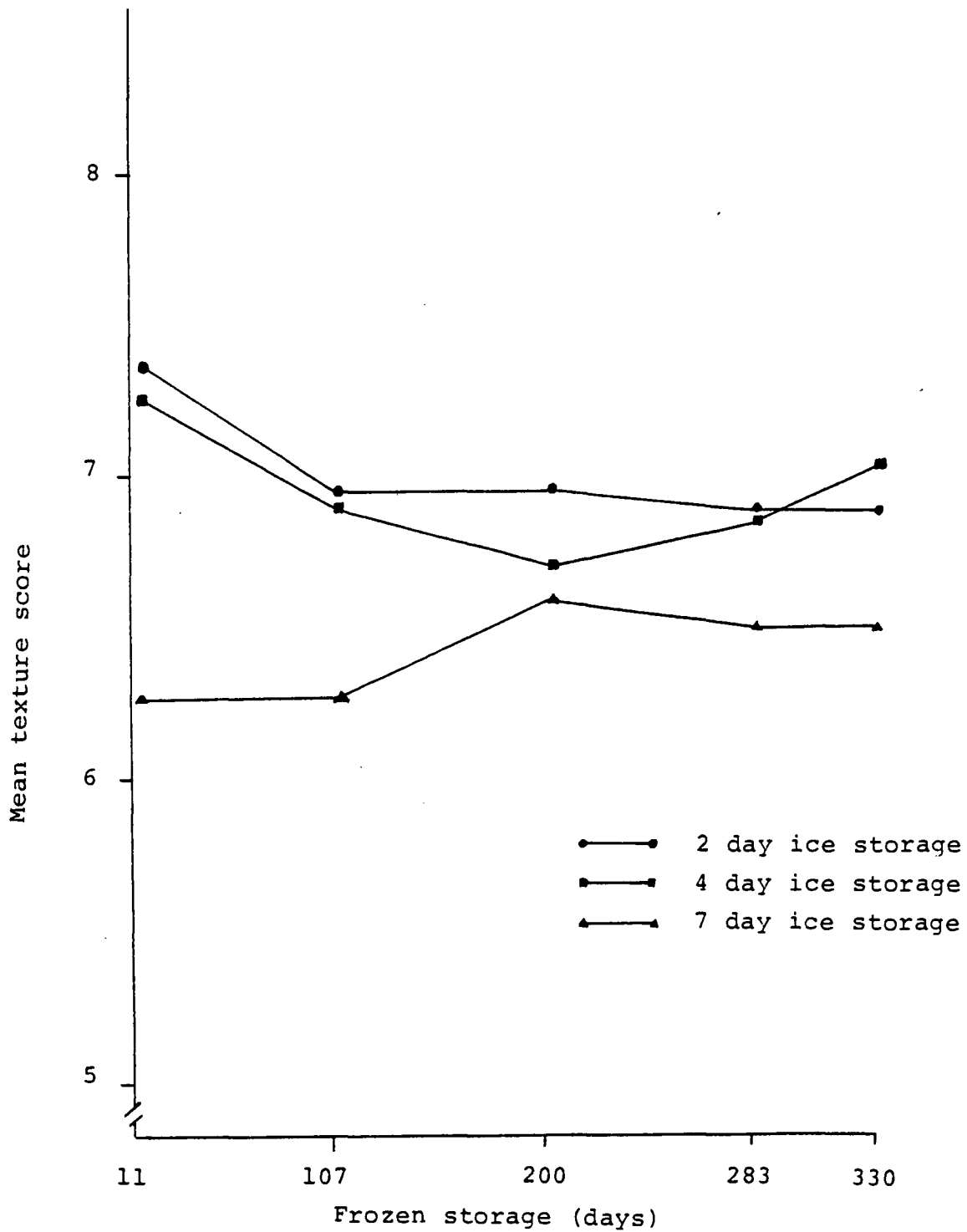


Figure 4. Mean texture scores of frozen cooked shrimp meat (condensed phosphate pretreatment)

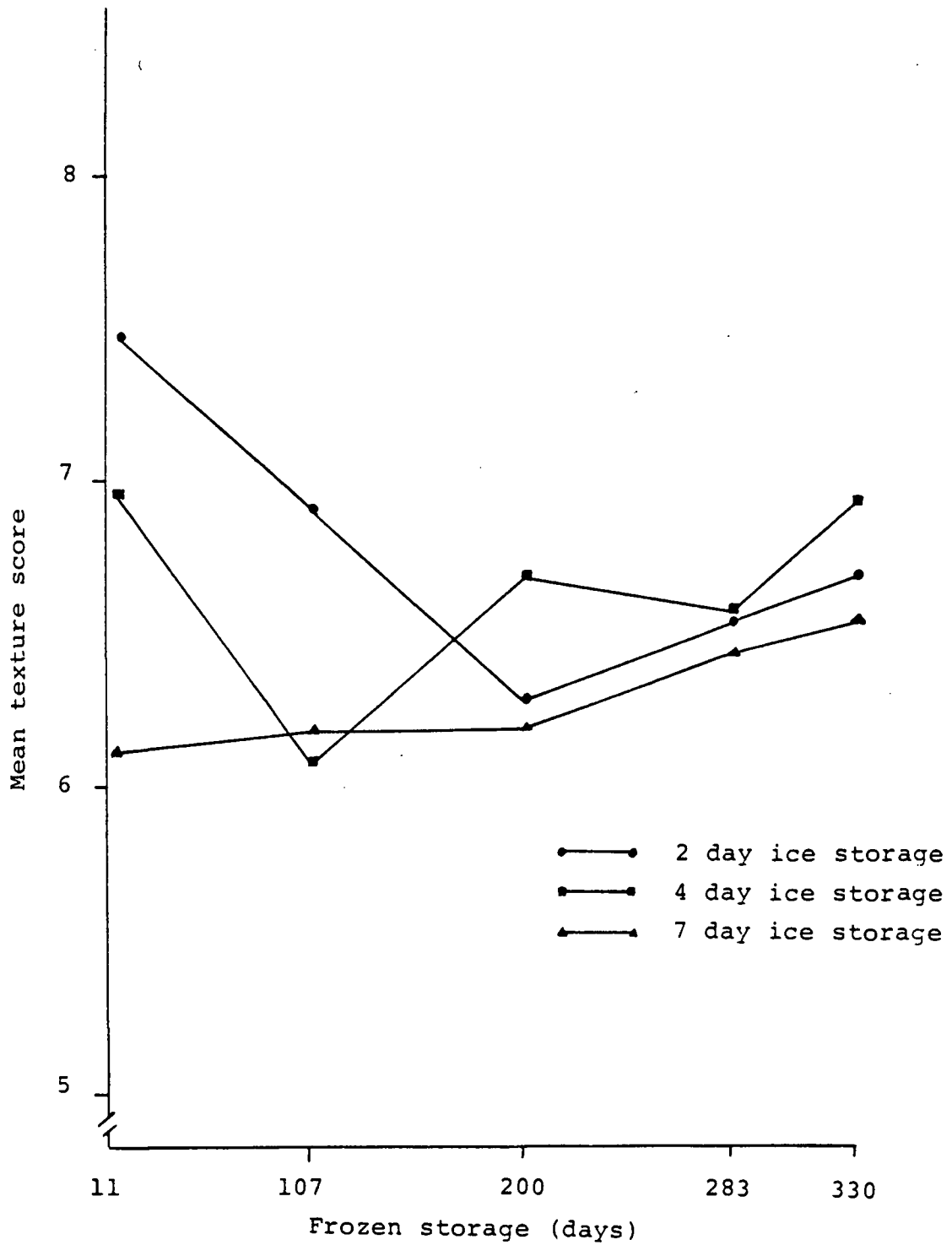


Figure 5. Mean texture scores of frozen cooked shrimp meat (control)

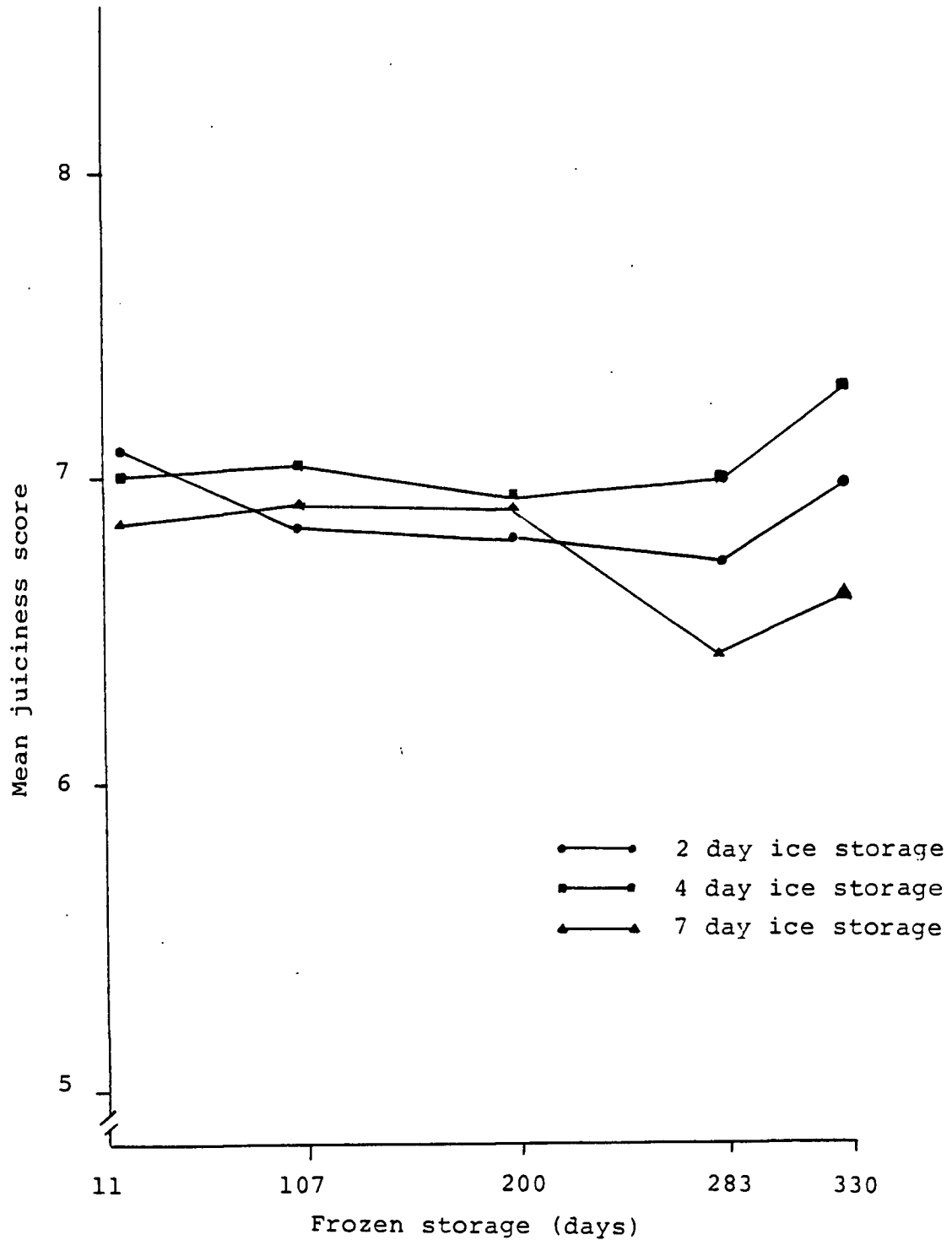


Figure 6. Mean juiciness scores of frozen cooked shrimp meat (condensed phosphate pretreatment)

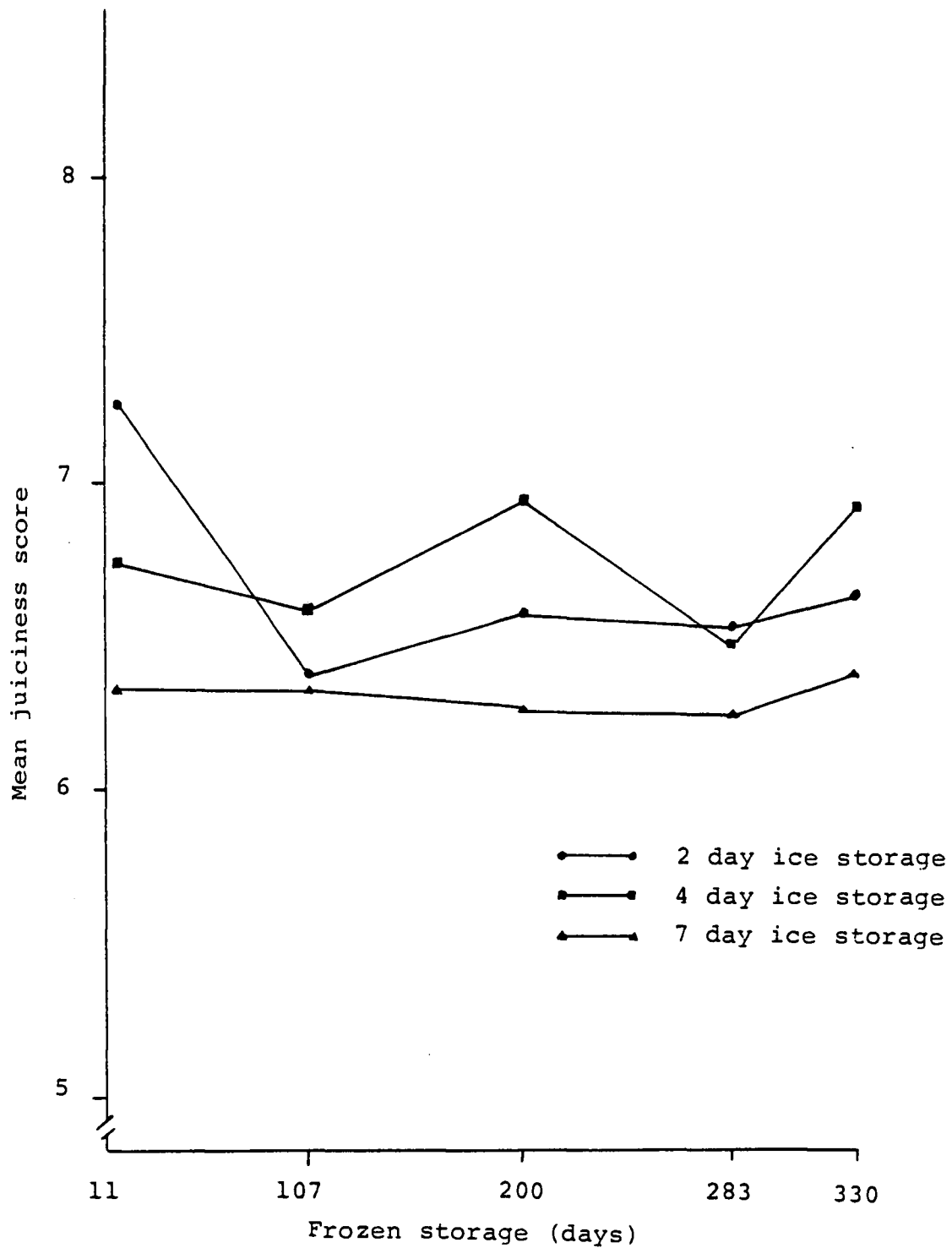


Figure 7. Mean juiciness scores of frozen cooked shrimp meat (control)

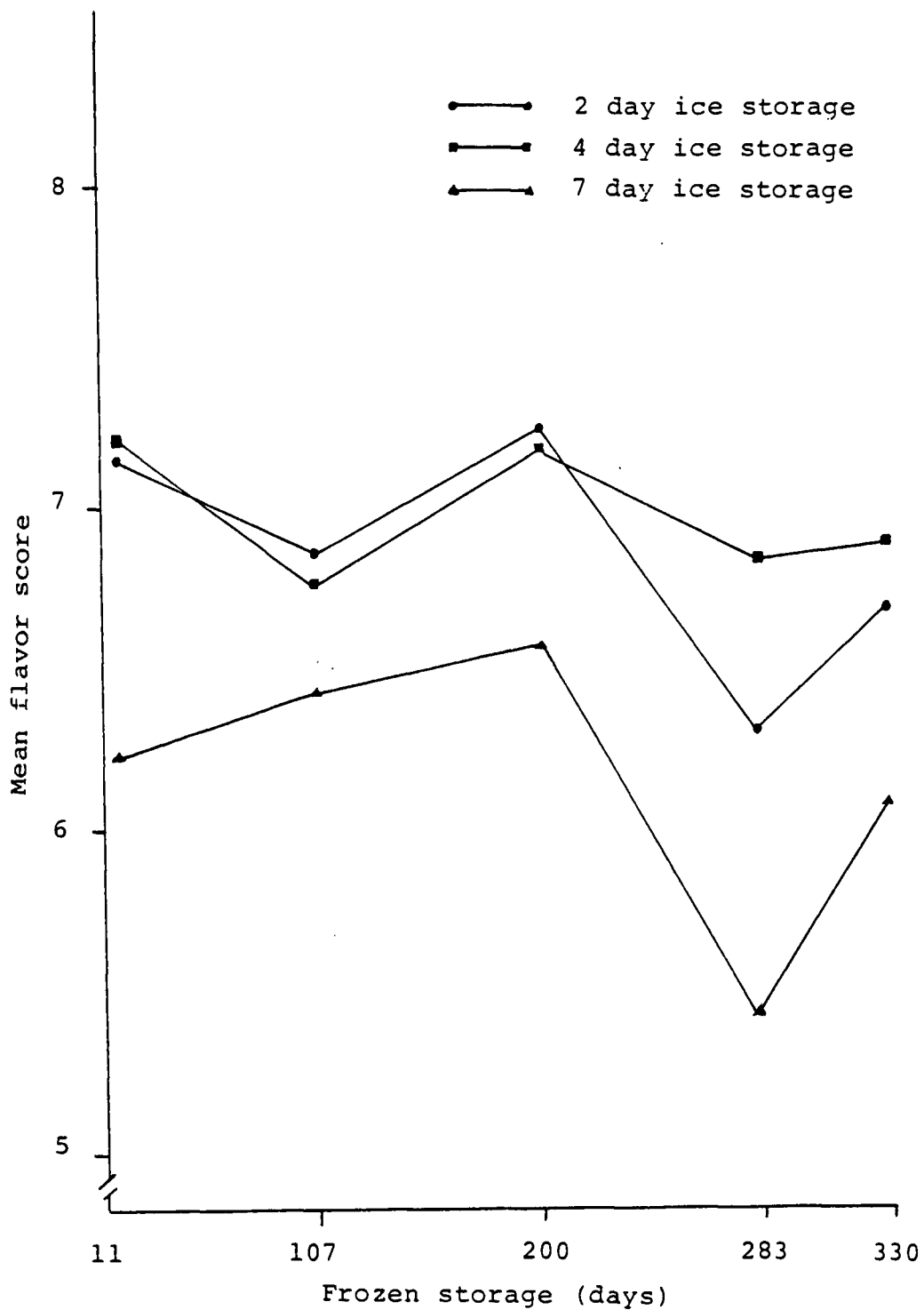


Figure 8. Mean flavor scores of frozen cooked shrimp meat (condensed phosphate pretreatment)

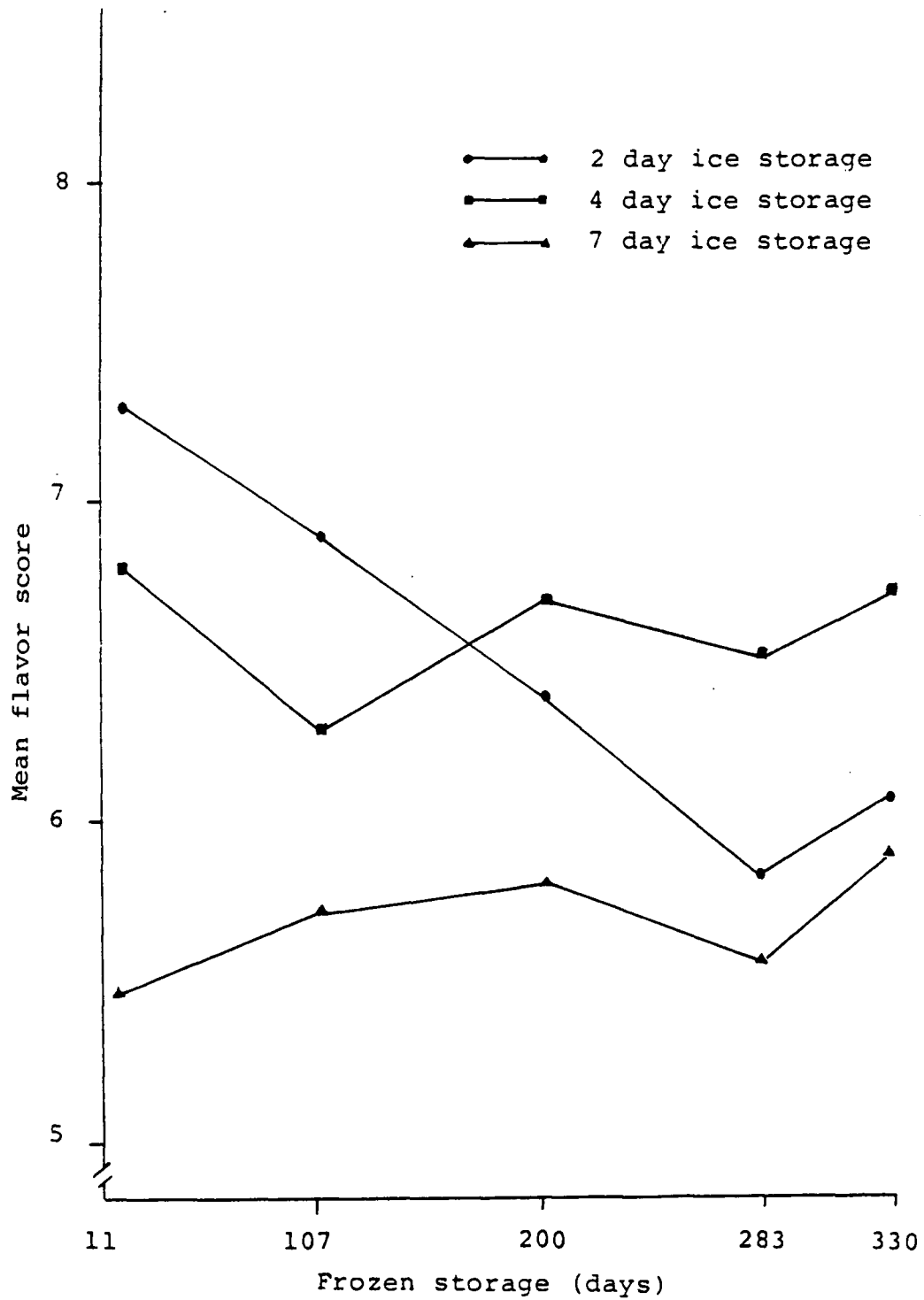


Figure 9. Mean flavor scores of frozen cooked shrimp meat (control)

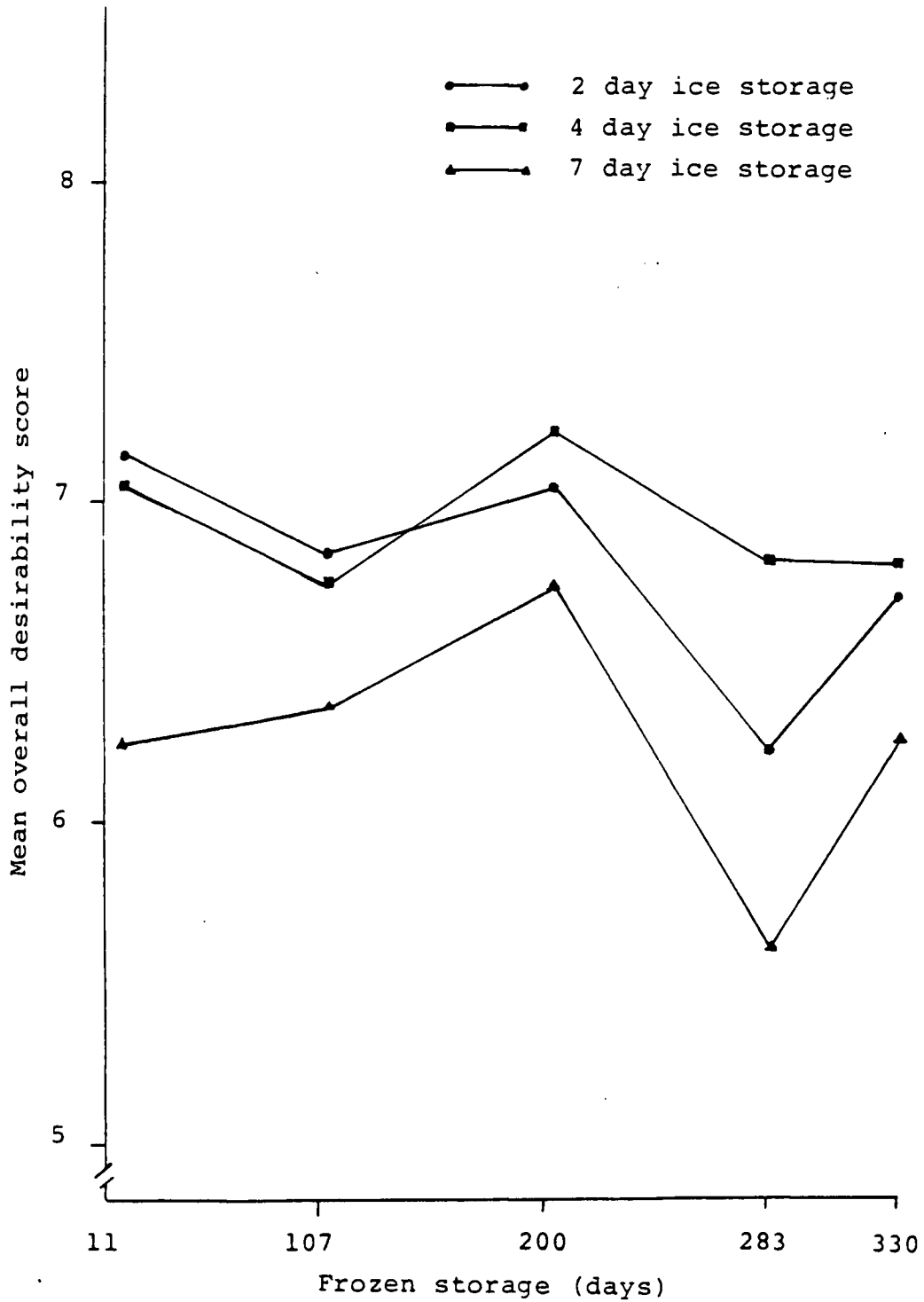


Figure 10. Mean overall desirability scores of frozen cooked shrimp meat (condensed phosphate pretreatment)

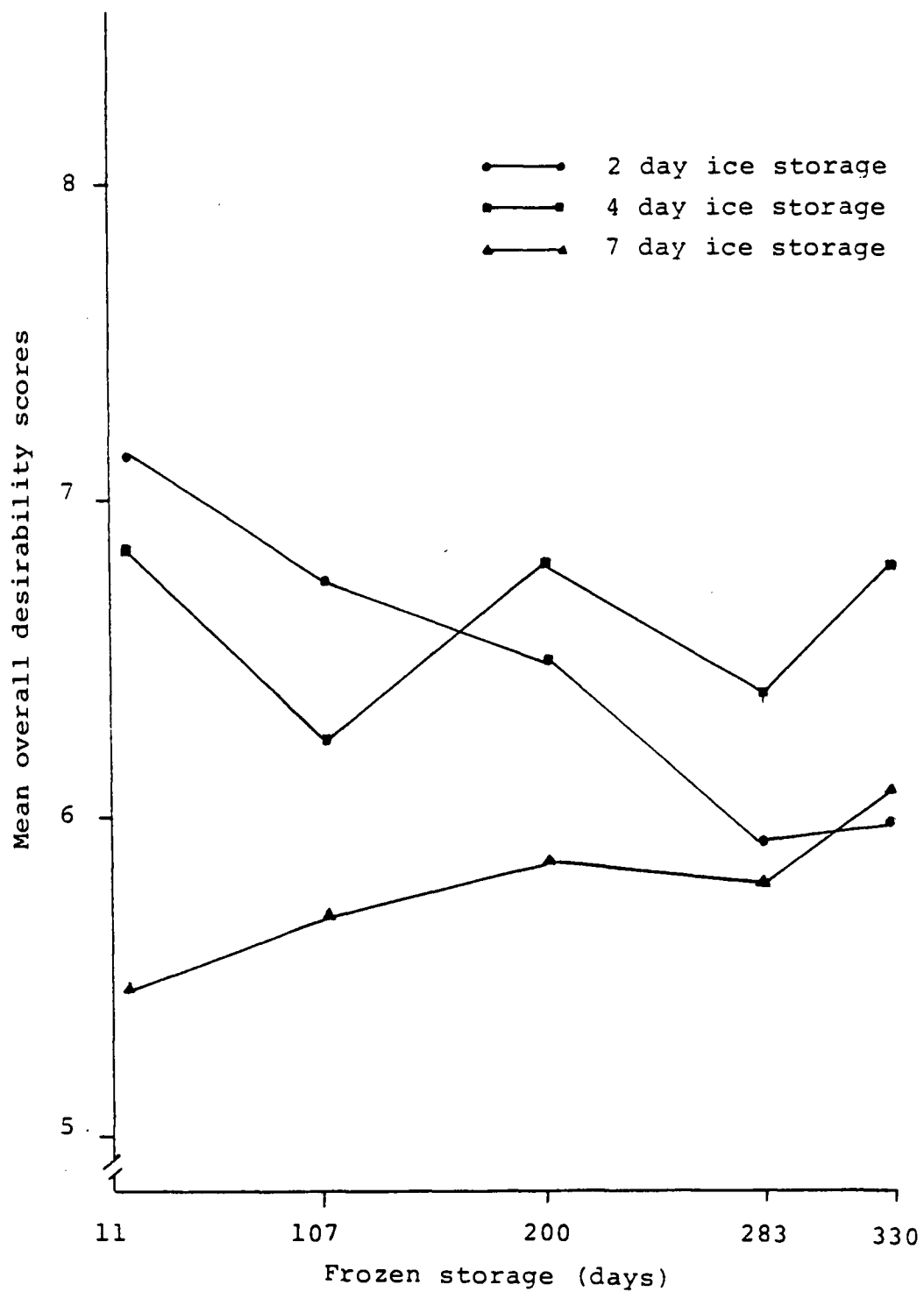


Figure 11. Mean overall desirability scores of frozen cooked shrimp meat (control)

SUMMARY AND CONCLUSIONS

Yield of cooked shrimp meat was improved by a condensed phosphate (6%) treatment at low temperature. During steam precooking, condensed phosphate interacted with collagen-like surface proteins to form a gelatinized layer which retarded the loss of fluid and soluble solid components. Polyphosphate-protein interactions were enhanced by the deterioration process induced in post-catch ice storage. This was reflected by the fact that condensed phosphate pretreated round shrimp had greater meat yields over respective control samples as ice storage was extended.

The significant difference in TMAO, TMA and DMA levels was found between condensed phosphate pretreated shrimp meat and respective control samples. These differences were related to the action of condensed phosphate treatment which retained a higher moisture content and retarded the loss of soluble solid material through steam precooking.

During extended ice storage, tyrosine and DMA contents increased while levels of TMAO and TMA in cooked meat were significant decrease through bacterial and enzymic degradations. Steam precooking and low temperature minimized these kinds of degradation in frozen storage. Changes in TMAO, TMA and DMA contents were speculated to be formed or degraded by non-enzymic mechanisms as frozen storage was extended.

The changes in TMA and DMA were significant with respect

to pretreatment, ice storage and frozen storage, but the levels were relatively low and still within the limits of acceptability set by Australia and Japan (Cobb and Vanderzant, 1975). This indicated that determination of TMA and DMA does not precisely reflect the quality of cooked meat during frozen storage.

Sensory evaluations for frozen cooked shrimp meat indicated that condensed phosphate pretreatment improved the color, texture, juiciness, flavor and overall desirability. The scores of sensory evaluations showed that a slight degradation occurred between 2 and 4 days of ice storage. At 7 days of ice storage, a relatively greater degradation of shrimp meat was detected by flavor panels. Factorial analyses of variance showed the F-values for the effects of frozen storage were relatively small and during frozen storage lack of progressive or non-significant changes in sensory scores indicated that the cooked shrimp meat could retain relatively high and uniform quality during frozen storage.

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