PHYSICAL AND CHEMICAL PROPERTIES OF SHRIMP DRIP AS INDICES OF QUALITY

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ABSTRACT

Physical and chemical characteristics of drip obtained from frozen-thawed shrimp were studied to determine if changes in these characteristics could be correlated with quality as determined by a taste panel. Shrimp were tested that had been stored (1) on ice followed by a minimum of frozen storage for the formation of drip, (2) at -10° F., and (3) both on ice and at -10° F.

The pH of the drip appeared to be a satisfactory objective quality index. Drip from shrimp considered "good" by the taste panel gave pH readings of 7.50 to 8.25, from shrimp considered "acceptable," from 8.26 to 8.40, and from shrimp considered "unacceptable," 8.41 and higher. The color and optical density of the drip changed correspondingly with quality, and objective measurements of the optical density could be made with a photoelectric colorimeter. Trimethylamine nitrogen content of shrimp drip showed good correlation with spoilage but gave no indication of the state of freshness of the unspoiled shrimp. The volume of drip collected and the nitrogen content of the drip were of little or no value as a quality index.

INTRODUCTION

The requirements of a freshness test for fishery products have been stated by Reay and Shewan (1949) as follows: (a) the test must be capable of sensitively and accurately estimating the product or products of spoilage, (b) the substance or substances measured should either be absent or should be present in constant concentration in the unspoiled sample, and (c) the substance or substances must increase or decrease regularly and rapidly once spoilage has started. In addition, to be most useful, the test should quantitatively indicate the loss of freshness of the product prior to the onset of organleptically detectable spoilage.

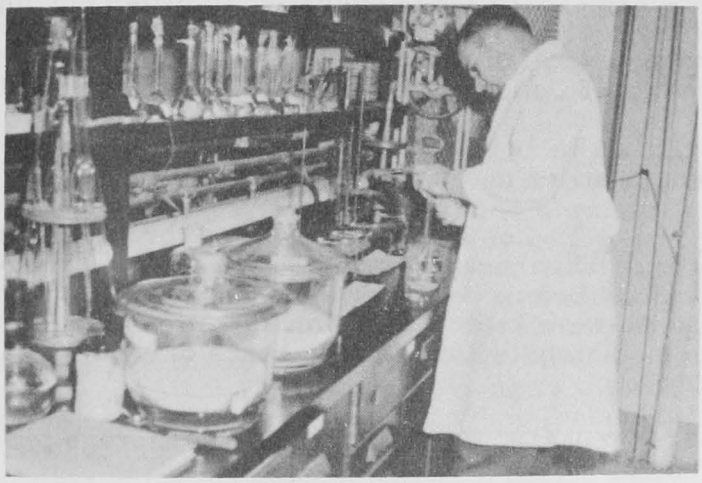

Fig. 1 - Preparing solutions for nitrogen determination.

Fieger and Friloux (1954) and Bailey, Fieger, and Novak (1956) found that bacterial counts and measurements of the content of trimethylamine nitrogen, volatile acids, and other constituents of shrimp tissue were not sufficiently sensitive to detect deterioration prior to spoilage. Measurements of pH and of amino nitrogen content of homogenized shrimp were of value in indicating loss of freshness, but the magnitude of change was small.

A more sensitive index might be obtained if shrimp drip fluids rather than shrimp tissue were tested. It is known that many products of spoilage tend to be water soluble. Thus, they may be lost with the drip that occurs when the tissues are thawed. Capture of the drip fluids might thus offer a concentrated source of spoilage products.

In the present study, therefore, various physical and chemical changes (amount of drip, pH, color, optical density, trimethylamine nitrogen, and Folin-Ciocalteu nitrogen) observed on the drip obtained by thawing frozen shrimp that had been held under varying conditions of storage were compared with organoleptic evaluations of quality of the shrimp to determine if a more satisfactory index of quality might be obtained by analyzing the drip rather than the shrimp tissue.

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EXPERIMENTAL METHODS

Table 1 presents a summary of samples, of storage procedures, and of organoleptic and physical and chemical tests. The details of the study were as follows:

Table 1 - Summary of Samples and Analyses

Data on Sample				Analyses Made On:						
				Shrimp Meat	Drip from Frozen Shrimp					
Lot Number	Species of Shrimp	Prestorage Handling	Storage Treatment	Organoleptic	pH	Color	Optical Density	Vol. of Drip	FC Nitrogen	TMA Nitrogen
1	Brown (Penaeus aztecus)	Commercial practice--about 3 days from water to laboratory	Iced for varying periods and then held frozen about 48 hours	X	X	X	-	X	X	-
			Stored at -10° F. for periods up to 6 months	X	X	X	-	-	-	-
			Iced for varying periods and then stored at -10° F. for 6 months	X	X	-	X	X	-	-
2	White (Penaeus setiferus)	Commercial practice--about 3 days from water to laboratory	Stored at -10° F. for periods up to 6 months	X	X	-	-	-	-	-
3	Brown (Penaeus aztecus)	Frozen within hours of capture. Thawed at start of experiment	Iced for varying periods and then held frozen about 48 hours	X	X	X	-	X	-	X

SAMPLES: Three lots of shrimp were used.

Lot 1: Lot 1 was composed of brown shrimp obtained from a commercial trawler at Brownsville, Tex. This lot was typical of the commercial catch in that it was a composite from several drags. The shrimp were packed in ice and shipped by air express to the laboratory at College Park, Md., where they arrived about 3 days after being caught.

Lot 2: Lot 2 was composed of white shrimp but was caught in the same area and otherwise handled in the same manner as was lot 1.

Lot 3: Lot 3 was another lot of brown shrimp from the same area. This lot was from a drag taken just before the boat returned to shore. The length of time that the shrimp were on deck before being headed and iced and the length of time on board the vessel before being landed were kept to a minimum. After the vessel arrived in port, the shrimp were frozen immediately (within several hours of catching) and were shipped to the laboratory packed in dry ice.

STORAGE PROCEDURES: The storage procedures used varied with the lot of shrimp tested.

Storage Procedure with Lot 1: The shrimp were divided into two sublots. Samples prepared from one sublot were glazed, those from the other were unglazed but overwrapped in moisture-vaporproof cellophane. Each sublot was divided into three groups, and each group was given a different storage treatment: treatment A (placed in iced storage), treatment B (placed in frozen storage), or treatment C (placed in iced and frozen storage).

TREATMENT A--ICED STORAGE: The shrimp were stored in ice for varying periods of time. Samples were randomly removed from the ice every 2nd or 3rd day for 14 days, and triplicate 10-ounce samples were packed in cartons and then frozen and either glazed or overwrapped. The freezing and glazing process required 48 hours and was necessary to condition the shrimp for the formation of drip. Two of the three samples were used for collection of drip, and the third was used for organoleptic testing.

TREATMENT B--FROZEN STORAGE: On arrival at the laboratory, the shrimp were packed in 10-ounce cartons, frozen, glazed or overwrapped, and placed in storage at -10° F.

Two cartons for collection of drip and one carton for organoleptic testing were removed monthly for 6 months.

TREATMENT C--ICED AND FROZEN STORAGE: The shrimp were stored in ice, as in treatment A. After being removed from iced storage, however, the samples were packaged, placed in storage at -10° F., and tested after 6 months.

Fig. 2 - Nitrogen determination.

Storage Procedure with Lot 2: Lot 2 was given the same storage procedure as was given lot 1 in treatment B.

Storage Procedure with Lot 3: Lot 3, after being thawed upon arrival at the laboratory, was given the same storage procedure as was given lot 1 in treatment A. No unglazed samples were prepared from this lot.

ORGANOLEPTIC PROCEDURES: The thawed shrimp were peeled, deveined, and added to 1½ pints of boiling water containing 3 teaspoons of salt, allowed to simmer for 5 minutes, removed, and allowed to cool before being served. A taste panel composed of five members was asked to judge whether the flavor and odor of the shrimp was "good," "acceptable," or "unacceptable." Numerical values of 3, 2, and 1, respectively, were assigned arbitrarily to the classifications for the purpose of treating the data quantitatively. Shrimp with a mean score of 2.3 or more were arbitrarily considered "good," those with a mean score of 2.2 to 1.7 were considered "acceptable," and those with a mean score below 1.7 were considered "unacceptable."

PHYSICAL AND CHEMICAL PROCEDURES: Volume of Drip: A standard method was developed for the collection of glaze and drip. Duplicate, frozen, 10-ounce blocks of shrimp were used. Each block was placed on a screen elevated about half an inch from the bottom of a 2-liter beaker, and the beaker was covered with "Saran Wrap" and placed in a water bath maintained at 100° to 120° F. This procedure kept the air temperature inside the beaker at 75° to 79° F., which was well below the protein-coagulation temperature of 113° F. reported by Frobisher (1946). From 45 to 60 minutes were needed to melt the glaze and separate the shrimp. As the glaze melted, it was removed periodically, leaving the shrimp still frozen. The glaze was assumed to be removed when the shrimp were no longer slippery to the touch. After the shrimp separated from the frozen block, each one was hung by the tail in a large funnel placed over a chilled graduate to collect the drip. Since no drip formed until the shrimp had been hung for 30 to 45 minutes, it can be assumed that little or no drip drained into the glaze during the time of separation of the shrimp. A standard period of 2 hours after complete removal of glaze was adapted for collection of drip.

pH Determinations: The pH of the drip was determined by means of a pH meter equipped with glass mercury electrodes. All determinations were made at room temperature (77° F.).

Color Changes and Optical Density: Color changes in drip were estimated visually. Optical densities were determined using a Klett-Summerson Colorimeter with a number 54 filter. This filter was chosen to obtain maximum sensitivity for the yellowish-colored drip samples.

Trimethylamine-Nitrogen (TMA-N): Trimethylamine-nitrogen was determined colorimetrically by the method of Dyer (1945). This method consists of extracting the trimethylamine salts with formalin, freeing the amine with potassium carbonate, and extracting the amine with toluene. The color is developed with picric acid in toluene solution. The optical density was read on a Beckman DU Spectophotometer at 410 millimicrons. The nitrogen con-

tent of a standard solution of trimethylamine-HCL was determined by a micro-Kjeldahl method.

Folin-Ciocalteu Nitrogen (FC-N): Nitrogen determinations were made colorimetrically by the modified method of Sutherland, Cori, Haynes, and Olsen (1949). This method is sensitive to protein nitrogen in very small amounts and is relatively simple to perform. The same Folin-Ciocalteu reagent has been used to measure protein decomposition in fish muscles (Wood, Sigurdsson, and Dyer 1942). The reagent reacts with aromatic phenolic compounds and trimethylamine (Dyer 1945). The intensity of the blue color resulting from the reaction of the reagent and the nitrogenous compounds contained in the drip was determined with a Beckman DU Spectrophotometer at 660 millimicrons. A solution of insulin, used as a standard, was assayed for its nitrogen content by the micro-Kjeldahl procedure.

COMPARISON OF ORGANOLEPTIC AND PHYSICAL AND CHEMICAL TESTS

The data from all tests were similar for the glazed and overwrapped sublots of shrimp. Therefore, only the results of the glazed samples are reported. Data for volume of drip, pH, TMA-nitrogen, and FC-nitrogen represent the mean of duplicate determinations.

VOLUME OF DRIP: Data on the volume of drip varied so erratically that no conclusions could be drawn. It was noted, however, that there seemed to be somewhat less drip from lot 3 shrimp than from those of lot 1, which would indicate that the special care given to preserve the quality of lot 3 shrimp may have reduced the amount of drip.

pH DETERMINATIONS: Iced Storage: The pH of shrimp drip increased regularly with increased time in iced storage and with decreased organolpetic quality (fig. 3). The decrease in organoleptic rating from "good" to "acceptable" for the lot 1 shrimp stored in ice came between the 7th and 8th day, and the decrease to "unacceptable" occurred after the 10th day of storage. The pH was 7.73 to 8.25 for drip from shrimp rated "good," 8.26 to 8.40 for drip from shrimp rated "acceptable," and 8.41 and higher for drip from shrimp rated "unacceptable."

The pH increased and organoleptic scores decreased much more gradually for lot 3 (fig. 3). The rate of spoilage was retarded, but when the quality of the shrimp dropped to "acceptable" on the 8th day, the pH of the drip was between 8.20 and 8.29. The drop in quality to "unacceptable" occurred on the 15th day at which time the pH of the drip was 8.44. Time required for quality changes in the various samples were in agreement with findings of Fieger and Friloux (1954), who showed that definite quality changes in shrimp occur after 7 days and 14 days iced storage, the latter period being when spoilage usually occurs.

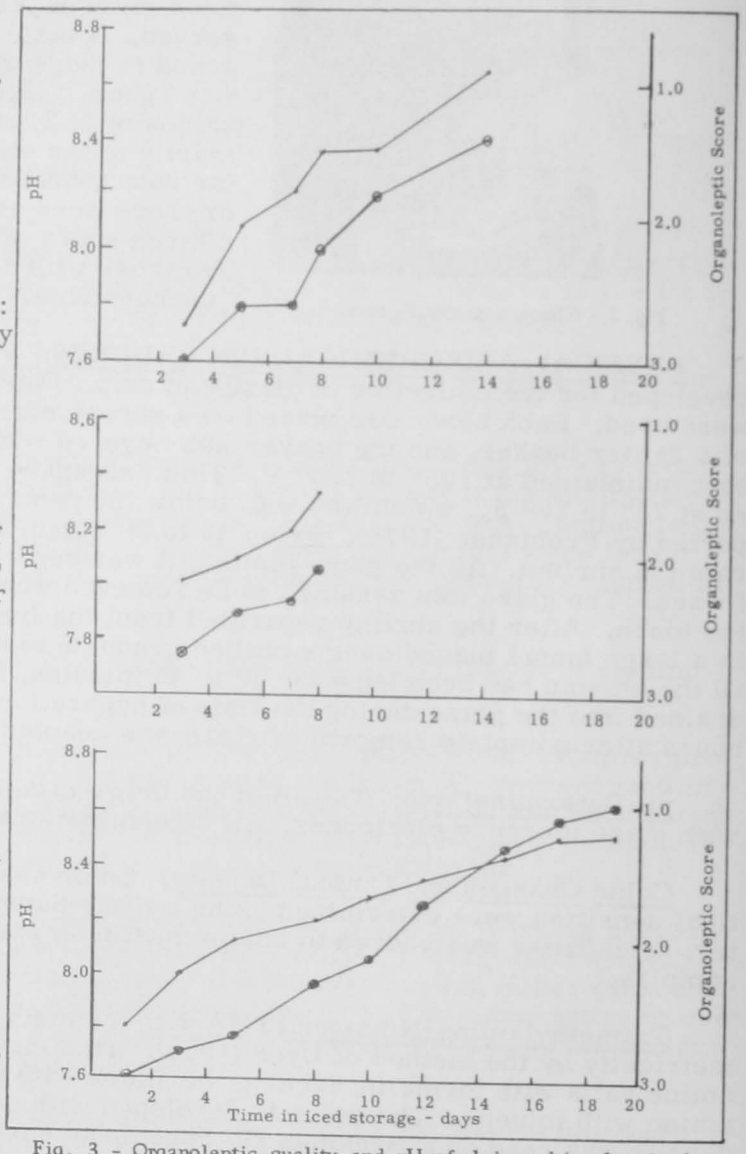

Fig. 3 - Organoleptic quality and pH of shrimp drip after iced storage and iced and frozen storage.

Frozen Storage: During the 6-months study of frozen storage, samples prepared from lot 1 (brown shrimp), and those from lot 2 (white shrimp), gave similar organoleptic scores and pH values for the drip. Both tests indicated that the shrimp remained of good quality during the entire period of testing. The data on lot 2 are presented in figure 4.

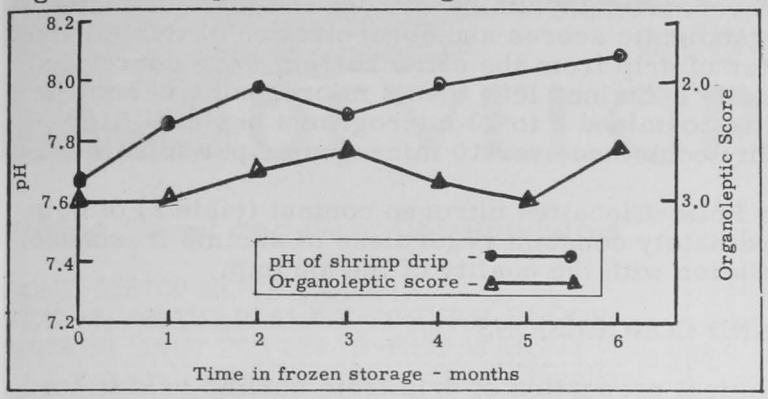

Fig. 4 - Organoleptic quality and pH of shrimp after frozen storage.

Combined Iced and Frozen Storage: Figure 3 also presents pH and organoleptic data for shrimp stored under the combination of iced and frozen storage. These pH values followed very closely those for the shrimp stored for the same time on ice but not held in frozen storage. The organoleptic scores for the samples frozen for 6 months were always slightly lower, however, than were those of shrimp tested before being frozen. Comments of the panel indicated a loss of flavor--that is, tastelessness rather than a presence of off-flavors and odors in the shrimp held in frozen storage. Thus, storage at -10° F. for periods up to 6 months does not materially affect the quality of properly-packaged shrimp, at least of the species tested.

COLOR CHANGES: With increased iced storage, the color of shrimp drip (table 2) changed in a regular manner from (a) almost transparent colorless, to (b) distinct translucent amber, to (c) opaque brown with suspended particles. These changes in shrimp drip appeared to correlate closely with changes in the quality of the shrimp. Drip that was almost

Table 2 - Some Physical and Chemical Properties of Shrimp Drip

Length of Iced Storage of Shrimp	Lot 1 After Iced Storage 1/			Lot 1 After Iced and Frozen Storage		Lot 3 After Iced Storage 2/		
	Amount of Drip Collected	Color of Drip	Folin-Ciocalteu Nitrogen	Amount of Drip Collected	Optical Density	Amount of Drip Collected	Color of Drip	Trimethylamine Nitrogen
Days	Milliliters		Milligrams Per Milliliter	Milliliters		Milliliters		Micrograms Per Milliliter
1	-	-	-	-	-	8.0	Transparent, colorless	3/<2.0
3	8.5	Transparent, colorless	1.5	12.5	0.318	7.8	Transparent, colorless	<2.0
5	9.8	Transparent, slight amber	2.9	14.0	0.356	7.5	Transparent, slight amber	<2.0
7	7.5	Transparent, distinct amber	2.2	12.5	0.426	-	-	-
8	10.0	Opaque, brown	2.0	11.0	0.554	6.8	Transparent, distinct amber	2.4
10	9.5	Opaque, brown	1.5	10.0	0.726	9.5	Opaque, brown	4.1
12	-	-	-	-	-	5.3	Opaque, brown	9.9
14	10.5	Opaque, brown suspended particles	2.4	-	-	-	-	-
15	-	-	-	-	-	5.5	Opaque, brown	17.6
17	-	-	-	-	-	5.6	Opaque, brown	31.9
19	-	-	-	-	-	6.0	Opaque, brown	35.3

1/The experiment was started approximately 3 days after the shrimp were caught.
2/The experiment was started approximately 1 day after the shrimp were caught.
3/Two micrograms per milliliter is limit of sensitivity.

colorless and transparent indicated "good" quality; drip that was distinctly amber and translucent indicated "acceptable" quality; and drip that was brown and opaque with suspended particles indicated "unacceptable" quality.

The optical density of shrimp drip (table 2) from lot 1 after iced and frozen storage showed a definite, steady increase during storage. More research work is warranted to test this characteristic of shrimp drip, since it appears to be promising as a quality index.

TRIMETHYLAMINE-NITROGEN: The trimethylamine-nitrogen content of drip (table 2) of shrimp from lot 3 showed limited correlation with organoleptic quality. This test did not reveal the loss of freshness prior to 8 days of iced storage, the trimethylamine-nitrogen concentration for the first 7 days being below 2 micrograms per milliliter of drip, the limit of sensitivity of the test. On the 8th day, however, trimethylamine-nitrogen could be detected, and thereafter, it increased regularly. Organoleptic scores and concentration of trimethylamine-nitrogen in micrograms per milliliter of drip from the same shrimp were correlated as follows: drip from shrimp of "good" quality contained less than 2 micrograms per milliliter, drip from those of "acceptable" quality contained 2 to 10 micrograms per milliliter, and drip from those of "unacceptable" quality contained over 10 micrograms per milliliter.

FOLIN-CIOCALTEU NITROGEN: The Folin-Ciocalteu nitrogen content (table 2) of drip from shrimp stored in ice remained approximately constant regardless of shrimp freshness. The results thus showed no apparent correlation with the quality of the shrimp.

SUMMARY AND CONCLUSIONS

Changes occurring in physical and chemical properties of drip from shrimp held in iced and frozen storage were studied for use as possible improved quality indices for the freshness of shrimp.

The pH and color changes of shrimp drip appeared to be satisfactory objective indices of shrimp quality. The pH appeared to be useful both as a spoilage test and as a freshness test to show the changes in quality before spoilage. This test was sensitive to changes before other objective tests were, such as trimethylamine-nitrogen. Color changes in drip followed a definite pattern from colorless and transparent for "good" quality shrimp, through amber and translucent for "acceptable" quality shrimp, to brown and opaque for "unacceptable" quality shrimp. Changes in optical density of shrimp drip increased with decrease in quality.

Trimethylamine-nitrogen was of no value as an indicator of prespoilage change in quality of shrimp, but it was a good indicator for the onset of spoilage. Determinations of volume of drip and of Folin-Ciocalteu nitrogen content of the drip were of no value as quality indices.

The pH of the drip was slightly higher than the pH of the whole shrimp, but the magnitude of the changes in pH when the shrimp changed from "good" to "acceptable" quality and then to "unacceptable" quality were no greater for the drip than for the whole shrimp as reported by Bailey, Fieger, and Novak (1956). The only advantage in the use of drip for taking pH measurements would therefore be that no equipment for homogenization is necessary, as it is for measurements on the whole shrimp. The observation of the color and transparency of the drip as an indication of quality would be useful under conditions where the usual laboratory equipment is lacking.

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