PHYSICAL AND CHEMICAL CHANGES OF PINK SHRIMP, *PANDALUS BOREALIS*, HELD IN CARBON DIOXIDE MODIFIED REFRIGERATED SEAWATER COMPARED WITH PINK SHRIMP HELD IN ICE

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ABSTRACT

Pink shrimp, *Pandalus borealis*, were held in carbon dioxide modified refrigerated seawater for 12.5 days and in ice for 11.5 days. Chemical tests for spoilage indicated that shrimp held in carbon dioxide modified refrigerated seawater were acceptable up to 9.5 days and those held in ice up to 6.5 days. Data on weight, yield, solids, carotenoids, protein, salt, and pH are given. When expressed on a constant basis (salt-free, 75% moisture), the yield of cooked product calculated from the gross weight of whole shrimp decreased rapidly during the first few days in either system. The yield of cooked meats from the carbon dioxide modified refrigerated seawater system decreased from 18.3% at 0.5 day to 15.3% at 4.5 days but varied in the ice system between 14.0 and 15.5% over the useful holding period of 6 days.

The advantages and disadvantages of the refrigerated seawater system (RSW) for holding fish and shellfish are well documented and were recently discussed by Barnett et al. (1971) and by Nelson and Barnett (1971). Based on bacteriological measurement and sensory evaluation, these authors showed that rockfish, *Sebastodes flavidus*, can be held in the RSW system modified by the addition of carbon dioxide (MRSW) for longer periods of time than in ice. The purpose of this study was to obtain detailed information on the physical and chemical changes that occur during time of holding of pink shrimp in the MRSW system compared with that of pink shrimp held in ice.

EXPERIMENTAL

Preparation of Pink Shrimp

Pink shrimp, *Pandalus borealis*, when received by the laboratory, had been held for 2 h at ambient temperature of -1.7°C (29°F) without ice aboard a commercial fishing vessel. Shrimp were separated from fish and after a brief rinse in cold freshwater were placed in fiber glass-coated hardware cloth baskets and rinsed again in cold tapwater for 2 min. The shrimp were then drained for 30 min and the weight of each sample was adjusted to contain 2,100 g (4.63 lb). It had been established that draining for 30 min resulted in nearly constant weight.

The MRSW holding portion of the experiment was conducted as follows. Baskets of shrimp and loose shrimp were alternately placed in the MRSW tank containing a 3.5% brine at -1.7°C, previously treated with carbon dioxide to 3.92 pH. The final loading ratio of shrimp to brine was 1:1.4 (wt/wt).

The ice holding portion of the experiment was conducted as follows. Samples of shrimp for ice holding were similarly rinsed, drained for 30 min, and adjusted to 2,100 g each before being placed in single layer cheese cloth "baskets" and covered with ice and 38.5 kg (85 lb) loose shrimp. Loose shrimp were mixed with ice to more closely simulate boat holding conditions. Fresh ice was placed on the ice-held samples daily to insure a minimum 15-cm (6-in) cover over any given sample.

Holding Tank and Refrigeration Unit

A 568-l (150-gal) fiber glass holding tank was connected to a refrigeration unit by three 3.81-cm (1½-in) flexible plastic hoses. The brine was circulated at 151 l/min (40 gal/min) through a shell and tube heat exchanger with the capacity to chill 454 kg (1,000 lb) of shrimp and brine from 10° to -1.7°C (50° to 29°F) in 3 h. Refrigeration was provided by a conventional Freon[2] 12 condensing unit. The

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[2]Reference to trade names does not imply endorsement by the National Marine Fisheries Service, NOAA.

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tubes in the heat exchanger were made of titanium to avoid corrosion. Carbon dioxide was metered into the suction side of the pump for maximum diffusion; at a rate of 0.2 l/min (0.2 ft^3/h), the pH was lowered from 7 to 4 in 5 h. In this 14-day experiment, 8.8 kg (4 lb) of carbon dioxide were used.

A chest-type home freezer was used as an insulated box to hold shrimp in ice. One day before its use the refrigeration was disconnected and the door raised to allow the ice to begin to melt in order to simulate conditions in a boat's hold.

SAMPLING

Sampling Procedure

In this comparative holding experiment, a sample was taken daily from each holding system and allowed to drain for 30 min before weighing (iced shrimp were first rinsed briefly in cold water to remove ice). Four subsamples were prepared from each sample—three to represent commercial practices and the fourth for laboratory analyses to determine chemical changes in the shrimp. The subsamples, stored at -34°C (-30°F) for later analyses, are as follows.

Subsampling Procedure

1. Whole shrimp: The total weight of whole shrimp was determined at each period of holding to simulate the weight of shrimp landed at the dock and to determine yield of products. Water uptake was determined by a solids analysis in a blended sample.
2. Hand-peeled, raw shrimp meats: This laboratory sample was used to determine basic chemical changes, mainly spoilage.
3. Hand-peeled, raw, washed shrimp meats: This sample simulated a machine peeled raw frozen product. Washing was required to approximate the leaching action of commercial machine peelers. The hand-peeled meats were washed gently in cold water for 2 min, drained on hardware cloth for 10 min, then weighed, and frozen for later analyses.
4. Hand-peeled, washed, cooked shrimp meats: This sample simulated a cooked frozen product. A portion of the washed meats after frozen storage, as in 3 above, was thawed and cooked in boiling water for 2 min at a 12:1 ratio, drained 1 min, cooled 5 min, and blended for analyses.

To prepare subsamples 2 and 3 for analyses, they were removed from the freezer left at room temperature for 2 h, stored in a refrigerator overnight to thaw, and then blended.

Analytical Techniques

After the frozen samples were thawed and blended, the following analyses were performed: total nitrogen, solids, total chloride (Horwitz 1975), total volatile base (TVB; Stansby et al. 1944), total volatile acid (TVA; Friedemann and Brook 1938), trimethylamine (TMA; Dyer 1945), and carotenoids (Kelley and Harmon 1972). Sodium and potassium were determined by using a Beckman Model B hydrogen-oxygen flame photometer on appropriate dilutions of a 20-g sample digested with nitric and perchloric acids. The pH of the brine was determined daily.

RESULTS AND DISCUSSION

Whole Shrimp

The change in weight of whole shrimp held in these systems has commercial importance. The yield of product obtained in a processing plant is calculated from the weight of whole shrimp landed at the dock. The time of holding and the holding system affect the weight of landed shrimp (Table 1) and, therefore, the yield of the final product. Whole shrimp held in MRSW gained 5% in gross weight during the first 1.5 days and slowly gained an additional 2% during the next 7 days. A much

TABLE 1.—Change in gross weight and percentage solids with time of holding 2,100 g of whole pink shrimp in modified refrigerated seawater (MRSW) and ice and pH of the brine.

		MRSW system		Ice system	
Holding time (days)	pH	Gross weight (g)	Solids (%)	Gross weight (g)	Solids (%)
0.5	6.85	2,173	22.1	2,215	20.7
1.5	6.50	2,198	18.8	2,333	18.6
2.5	6.40	2,191	19.0	2,333	17.6
3.5	6.40	2,165	18.8	2,365	18.7
4.5	6.10	2,214	18.6	2,330	17.5
5.5	6.30	2,214	18.0	2,323	17.2
6.5	6.40	2,212	18.3	2,355	16.8
7.5	6.35	2,226	18.0	2,315	16.9
8.5	6.30	2,250	18.3	2,331	17.1
9.5	6.50	2,200	17.8	2,254	16.0
10.5	6.70	2,177	17.6	2,263	16.3
11.5	6.67	2,245	17.7	2,239	14.5
12.5	6.57	2,221	17.7		

higher gain in weight was observed in the ice-held shrimp. The ice-held whole shrimp gained 11% in the first 1.5 days, maintained this weight for 8.5 days, and decreased thereafter. These gross changes in weight were caused by changes in the water, solids, and salt content of whole shrimp with time of holding (Collins 1960, 1961).

The pH of the brine was 3.92 at the beginning of the experiment and rose to 6.85 during the first 12 h but varied between 6.1 and 6.9 during the remainder of the experiment. The flow of carbon dioxide was regulated at approximately 0.2 l/min but was shut off occasionally to reduce excess loss of carbon dioxode to the environment and buildup of foam.

Hand-Peeled, Raw, Pink Shrimp Meats

Gross weights of hand-peeled, raw meats increased rapidly in both holding systems (Table 2). The salt and sodium content of the raw peeled meats from the MRSW system increased rapidly during the first 2 days to 2% and 0.85%, respectively, and remained at this level over the remainder of the holding period. Potassium decreased during the holding period (MacLeod et al. 1960). In the ice system, however, the meats slowly lost salt, presumably due to the leaching effect of the ice melt.

Based on chemical tests, the quality of shrimp held in the MRSW system was considered acceptable through 9.5 days. There was a slight increase in the total volatile acid value at 9.5 days and in the trimethylamine value at 10.5 days, suggesting that quality deteriorated slightly after 8.5 days. In the ice system, quality was acceptable up to 6.5 days, borderline at 7.5 days, and unacceptable thereafter.

Because of the large excess of ice used in this holding experiment, the commercial limit for holding shrimp on ice would probably be less than 6.5 days. In this study, it appears that pink shrimp held in the MRSW system can be held for several days longer than in ice.

Hand-Peeled, Raw, Washed, Pink Shrimp Meats

The solids content (Table 3) for the hand-peeled, raw, washed meats when expressed as percentage composition, was nearly equal from the two holding systems after the effects of salt were removed by subtraction. In both systems there was a rapid decrease in percentage solids (increased moisture) for the first 5 days, but the percentage solids remained about equal thereafter. Salt, sodium, and potassium followed the same trend as the raw, peeled meats but at a lower level due to the washing.

The data on gross weight and composition (Table 3) are not useful for direct comparison of recovery of meat between the two holding systems because of differences in moisture and salt content. When recalculated on a constant basis (salt-free, 84% moisture), recoveries of raw, washed meats were much higher for the ice system than for the MRSW system (Figure 1). This observation was confirmed when recoveries of protein were compared for the two systems (Figure 1). The sharp drop in recovery at 6.5 days for the ice system suggested that soluble proteins were retained through the mild washing technique used in this experiment until spoilage became evident (the 6.5 day break point). In the MRSW system, however, the soluble proteins were leached gradually into the aqueous system.

TABLE 2.—Change in weight and analytical values with time of holding 2,100 g of hand-peeled, raw, pink shrimp meats in modified refrigerated seawater (MRSW) and ice.

	MRSW system								Ice system							
Holding time (days)	Gross weight (g)	Solids (%)	NaCl (%)	Na (%)	K (%)	TVA (meq H+/ 100 g)	TVB (mg N/ 100 g)	TMA (mg N/ 100 g)	Gross weight (g)	Solids (%)	NaCl (%)	Na (%)	K (%)	TVA (meq H+/ 100 g)	TVB (mg N/ 100 g)	TMA (mg N/ 100 g)
0.5	759	19.6	1.5	0.66	0.16	0.04	10.2	0.1	743	19.0	0.6	0.26	0.27	0.10	11.0	0.0
1.5	797	19.0	1.9	0.78	0.10	0.05	4.8	0.3	787	18.0	0.5	0.26	0.25	0.10	4.0	0.3
2.5	790	18.3	2.0	0.83	0.09	0.06	2.8	0.3	815	17.1	0.5	0.25	0.21	0.08	4.5	0.2
3.5	803	18.0	2.1	0.85	0.08	0.16	7.2	0.2	819	16.9	0.6	0.26	0.21	0.06	8.8	0.2
4.5	807	17.7	2.1	0.85	0.08	0.28	7.0	0.4	827	16.5	0.6	0.25	0.21	0.21	10.8	0.2
5.5	793	17.5	2.1	0.84	0.09	0.26	7.0	0.6	822	16.6	0.6	0.26	0.20	0.15	10.9	0.3
6.5	812	17.5	2.2	0.85	0.09	0.39	6.6	0.5	830	15.7	0.5	0.24	0.18	0.32	12.4	0.3
7.5	814	17.6	2.2	0.84	0.08	0.31	7.2	0.5	837	15.7	0.5	0.23	0.18	0.46	12.8	1.1
8.5	822	17.5	2.2	0.90	0.09	0.21	7.0	0.8	853	15.9	0.5	0.24	0.18	0.51	18.5	3.2
9.5	812	17.3	2.2	0.90	0.09	0.43	6.8	0.8	855	15.2	0.4	0.20	0.15	0.58	18.9	5.1
10.5	805	17.1	2.2	0.90	0.09	0.40	7.3	1.1	850	15.2	0.5	0.21	0.16	0.87	26.2	11.4
11.5	836	16.9	2.2	0.91	0.09	0.50	9.1	1.1	848	13.0	0.2	0.11	0.07	0.50	15.8	6.5
12.5	827	16.3	2.1	0.85	0.08	0.46	7.5	1.1								

TABLE 3.—Change in weight and analytical values with time of holding 2,100 g of hand-peeled, raw, washed, pink shrimp meats in modified refrigerated seawater (MRSW) and ice.

	MRSW system						Ice system					
Holding time (days)	Gross weight (g)	Solids (%)	Protein (%)	NaCl (%)	Na (%)	K (%)	Gross weight (g)	Solids (%)	Protein (%)	NaCl (%)	Na (%)	K (%)
0.5	749	17.8	15.4	1.2	0.48	0.14	761	16.4	15.2	0.5	0.21	0.20
1.5	827	17.6	13.7	1.7	0.65	0.08	820	15.9	14.7	0.5	0.21	0.19
2.5	816	16.6	13.6	1.8	0.69	0.07	844	15.3	14.1	0.4	0.21	0.17
3.5	783	16.5	13.5	1.8	0.70	0.07	862	15.1	13.8	0.5	0.22	0.16
4.5	799	16.1	13.1	1.9	0.71	0.07	859	14.9	13.8	0.5	0.22	0.16
5.5	809	15.8	12.8	1.9	0.69	0.06	859	15.0	13.9	0.5	0.25	0.17
6.5	812	16.1	12.9	1.9	0.73	0.07	846	14.3	13.1	0.4	0.21	0.14
7.5	801	16.4	13.3	1.9	0.69	0.07	856	14.3	13.3	0.4	0.20	0.14
8.5	828	16.2	13.0	1 9	0.70	0.07	866	14.4	13.2	0.4	0.20	0.14
9.5	794	16.1	13.1	2.0	0.71	0.07	864	13.9	12.6	0.4	0.17	0.12
10.5	793	15 9	11.1	2.0	0.72	0.07	850	14.0	12.8	0.4	0.17	0.13
11.5	807	15.7	12.6	2.0	0.71	0.07	825	12.2	11.2	0.2	0.09	0.05
12.5	796	16.0	12.8	2.1	0.75	0.07						

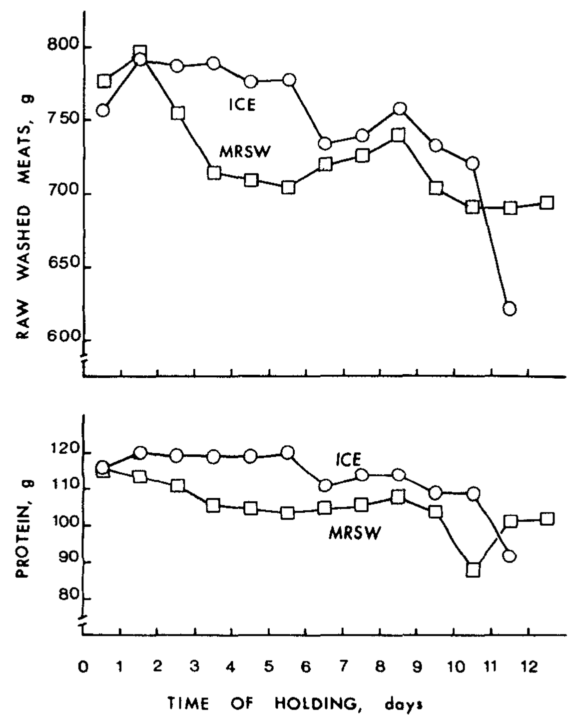

FIGURE 1.—Recovery of hand-peeled, raw, washed pink shrimp meats with time of holding 2,100 g of shrimp in modified refrigerated seawater (MRSW) or ice, expressed on a salt-free, 84% moisture basis and protein.

Commercial shrimp peelers exert a strong mechanical and washing action on the shrimp, which leaches out soluble proteins. In part therefore, the final yield would be a function of the gross weight of the landed whole shrimp and of the amount of soluble protein present, which would be influenced by the time and extent of action by bacteria or enzymes. Because the MRSW system reportedly extends holding time, ex-vessel shrimp—processed at an equal stage of quality (say, 4-day ice and 8-day MRSW) and at an equal water content—should give equal yields. In actual practice, however, machine peeling efficiency tends to be the controlling factor for yield. For example, if shrimp were to peel too easily on the machines, yields would be low because the meats would be rubbed off on the rollers. Yields would also be low if the shrimp were too difficult to peel because some unpeeled shrimp would be discarded at the inspection belt. Nelson and Barnett[3] obtained a 19% raw meat yield from pink shrimp held in the MRSW system and processed through a Laitram (Model A) machine peeler.

Hand-Peeled, Washed, Cooked, Pink Shrimp Meats

The gross weights for hand-peeled, washed, cooked meats obtained from the 2,100 g of whole shrimp were considerably higher from the ice-held shrimp than from the MRSW-held shrimp (Table 4). Under commercial processing conditions, infill weights must be adjusted to compensate for the high moisture content which would otherwise cause low drained weights after retorting or freezing. Consequently, to equalize the variable water content between holding systems and samples, we calculated the weight on a constant basis (salt-free, 75% moisture) and found that the two holding systems gave nearly identical recoveries except for low recoveries during the first several days in

[3]Nelson, R. W., and H. J. Barnett. Improved shrimp quality by the use of RSW modified with CO_2 gas. Unpubl. manuscr. Northwest and Alaska Fisheries Center Utilization Research Division, NMFS, NOAA, 2725 Montlake Boulevard East, Seattle, WA 98112.

TABLE 4.—Change in weight and analytical values with time of holding 2,100 g of hand-peeled, washed, cooked, pink shrimp meats in modified refrigerated seawater (MRSW) and ice.

	MRSW system							Ice system						
Holding time (days)	Gross weight (g)	Solids (%)	Protein (%)	Carotenoid index	NaCl (%)	Na (%)	K (%)	Gross weight(g)	Solids (%)	Protein (%)	Carotenoid index	NaCl (%)	Na (%)	K (%)
0.5	413	24.8	22.3	0.065	0.7	0.35	0.09	353	24.2	22.6	0.047	0.3	0.16	0.14
1.5	389	25.6	22.6	0.077	1.1	0.49	0.06	395	23.3	21.5	0.062	0.3	0.17	0.14
2.5	352	27.6	24.1	0.089	1.2	0.49	0.05	390	22.6	20.5	0.058	0.3	0.17	0.13
3.5	284	28.1	24.6	0.084	1.1	0.46	0.04	373	22.4	20.9	0.067	0.3	0.17	0.12
4.5	309	28.6	24.6	0.089	1.1	0.46	0.04	399	21.6	20.1	0.064	0.3	0.16	0.11
5.5	286	29.6	25.8	0.091	1.1	0.46	0.04	367	23.1	21.3	0.068	0.3	0.17	0.12
6.5	298	30.2	26.1	0.086	1.1	0.43	0.04	374	22.0	20.3	0.068	0.3	0.16	0.13
7.5	280	29.9	26.9	0.092	1.1	0.42	0.04	383	21.9	20.0	0.074	0.3	0.15	0.10
8.5	289	29.9	25.6	0.098	1.1	0.43	0.04	398	22.0	20.2	0.074	0.3	0.16	0.11
9.5	291	29.8	25.7	0.096	1.1	0.46	0.04	396	21.8	20.0	0.075	0.2	0.16	0.08
10.5	275	30.5	26.6	0.093	1.1	0.44	0.04	387	21.5	19.9	0.077	0.2	0.14	0.09
11.5	258	30.0	26.4	0.090	1.1	0.44	0.04	348	21.8	19.9		0.1	0.13	0.09
12.5	262	29.9	26.1	0.094	1.1	0.44	0.04							

ice caused by poor peeling characteristics. These adjusted weights and the protein data (Figure 2) showed a rapid decrease from both holding systems to 4.5 days, a leveling off to 10.5 days, and another decrease at 11.5 days.

Under commercial fishing and processing conditions, payment for landed shrimp is based on weight, and weight depends upon time of holding and system used. In our equipment, ice-held shrimp gained more weight and gave a greater recovery of cooked meats than shrimp in the MRSW system. Based on the weight of whole shrimp (Table 1) and the weight of cooked meats (Table 4), therefore, MRSW-held shrimp gave much lower yields than ice-held shrimp, averaging 13.9 and 16.4%, respectively. This difference in yield between systems would be reduced when the processor adjusts the weight of infill for a proper cut-out weight. Overall, the only difference in yield between systems is that caused by changes in water and salt content in the whole shrimp, i.e., landed weight. Under production conditions, MRSW has a slight advantage over ice because whole shrimp gain less in MRSW than in ice. It is believed that the laboratory data on the MRSW system would be representative of an MRSW holding system on a boat, but icing techniques may vary considerably from laboratory to boat, and the results obtained in the laboratory may differ from those in commercial practice.

Sodium chloride, sodium, and potassium followed the same general trends as the previous subsamples. The lower levels (1.1% NaCl, MRSW; 0.3% NaCl, Ice) were caused by cooking.

The carotenoid index, previously used to indicate comparative quality between production variables (Collins and Kelley 1969), showed an increase with increase in time of holding shrimp in

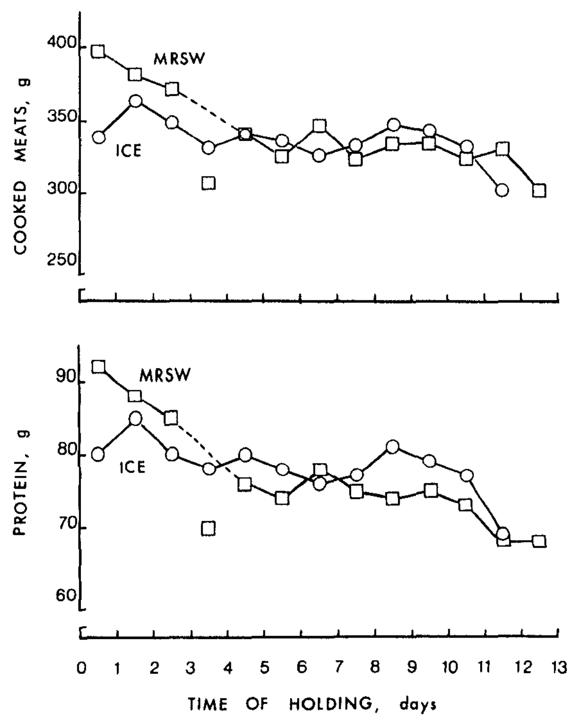

FIGURE 2.—Recovery of hand-peeled, cooked pink shrimp meats with time of holding 2,100 g of shrimp in modified refrigerated seawater (MRSW) or ice, expressed on a salt-free, 75% moisture basis and protein.

both systems. The index, expressed on a dry basis, unexpectedly increased rather than decreased with holding time. We suggest that the peeling-washing technique used in this experiment was less severe than that used during commercial machine peeling and that the 26% loss of protein in cooked meats over the holding period caused a pseudoincrease in the carotenoid content. In agreement with Nelson and Barnett (1971), the color of shrimp held in MRSW was much better than that for shrimp held in ice.

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