

WALLEYE POLLOCK, *THERAGRA CHALCOGRAMMA*: PHYSICAL, CHEMICAL, AND SENSORY CHANGES WHEN HELD IN ICE AND IN CARBON DIOXIDE MODIFIED REFRIGERATED SEAWATER

KERMIT D. REPPOND, FERN A. BULLARD, AND JEFF COLLINS¹

ABSTRACT

Walleye pollock, *Theragra chalcogramma*, were held in the round in ice and in CO₂ modified refrigerated seawater and periodically examined for physical and chemical changes as well as changes in the palatability of baked portions of blocks of fillets. Taste panel evaluation revealed that satisfactory fillets were obtained from fish that would have been judged spoiled if based on examination of the fish in the round. Sensory evaluation of baked fillet portions indicated that fish were acceptable for consumption to 6 days if heavily iced. The fish held in modified refrigerated seawater were judged acceptable only to 4 days because of lower sensory scores for salt content and flavor. Yield of fillets and protein content did not change significantly with time of holding in either medium. The total volatile acid and trimethylamine data indicated that these tests may prove useful as chemical indicators of spoilage for ice-held fish whereas determination of trimethylamine oxide or extractable protein nitrogen may prove useful for fish held in modified refrigerated seawater. Round weight and dimethylamine content increased in fish from both systems with time of holding as did the salt content of fish held in modified refrigerated seawater. Total volatile base, formaldehyde, and free α -amino-nitrogen content remained unchanged but nonprotein nitrogen and total solids content decreased with time of holding.

Walleye pollock, *Theragra chalcogramma*, have been the subject of several studies concerning changes that occur in frozen storage, and how these changes affect the suitability of pollock in traditional Japanese products (Iwata and Okada 1971, Okada and Noguchi 1974). Uchiyama et al. (1972) and Kramer et al. (1977) reported on changes that occur when pollock are held in ice. If pollock are to be held more than a few hours, ice or some type of refrigeration is needed to retard deterioration in quality. The advantages and disadvantages of refrigerated seawater (RSW) for holding fish and shellfish are well established (Roach et al. 1967). In recent years, reports have appeared on holding fish or shrimp in RSW modified by the addition of dissolved CO₂ (MRSW) (Barnett et al. 1971; Bullard and Collins 1978). These authors reported that deterioration occurred at a slower rate in MRSW than in ice. Lemon and Regier (1977) noted similar results with Atlantic mackerel, *Scomber scombrus*, held in either ice, RSW, or MRSW. Experiments with Atlantic ocean perch, *Sebastes marinus*, (Longard and Regier 1974) also confirmed the superiority of MRSW over RSW or ice as a holding medium. The objec-

tives of this study were to generally characterize the changes that occur in walleye pollock with time of holding in ice and in MRSW, to determine which holding medium is superior, and to determine if some of the common chemical indices for spoilage could be useful for pollock.

METHODS

Sampling

A catch of various species of bottom fish including approximately 135 kg each of walleye pollock and Pacific cod, *Gadus macrocephalus*, was made on 2 November 1976 by the RV *Oregon* near Cape Barnabas, Kodiak Island, Alaska, and shall be referred to as Lot 1. Lot 1 was evaluated by physical and chemical methods and by informal subjective observation on whole fish and their raw fillets. No formal sensory evaluation of cooked pollock was possible because of the limited amount of fish. To obtain fish for formal sensory evaluation, a second catch was made 1 yr later on 13 October 1977 at the same location and shall be referred to as Lot 2. Most of the chemical analyses conducted on Lot 1 were repeated on Lot 2 to see if the lots were similar. Analyses for total volatile base (TVB) and free α -amino acids were conducted on

¹Northwest and Alaska Fisheries Center, National Marine Fisheries Service, NOAA, P.O. Box 1638, Kodiak, AK 99615.

Lot 1 only. Analyses for dimethylamine (DMA), trimethylamine oxide (TMAO), and formaldehyde (FA) were conducted on Lot 2 only. Analyses for total volatile acid (TVA), trimethylamine (TMA), total nitrogen, total solids, chloride, extractable protein nitrogen (EPN), and nonprotein nitrogen (NPN) were conducted on both lots.

Fish in Lot 1 were held on a sorting table until arrival at the laboratory 6 h later. Ambient air temperature was about 4° C. Pollock and cod were separated from the rest of the catch, individually weighed, tagged, and transferred to the previously described ice or MRSW systems (Bullard and Collins 1978). To simulate a commercial operation, the pollock and cod were not segregated by species within the holding systems. This paper deals with pollock; cod will be discussed in a subsequent article. At regular intervals up to 15½ days, pollock were selected in such a manner that the average weight per fish in a particular sample was close to the average for all the pollock (495 ± 175 g SD). Each sample from the ice system consisted of 13 fish and each sample from the MRSW system consisted of 14 fish.

Prior to loading with fish, carbon dioxide was injected into the refrigerated brine until the pH leveled off at 4.3. Subsequent intermittent addition of carbon dioxide kept the pH between 5 and 6 throughout the experiment. Temperature was maintained at -1° C. The brine to fish ratio was 1.5:1. In the ice system, the fish were mixed in a fivefold excess of ice and fresh ice was added as necessary to replace melted ice. Great care was taken to insure the fish did not touch each other. Although commercial icing conditions are not as thorough, this procedure was used so the data obtained would be based on ideal icing conditions. A control sample was taken 6 h after arrival at the dock.

After removal of a sample from a holding system, the fish were washed briefly to remove slime or ice, drained on a rack for 5 min, and the weight of the individual fish recorded. The fish were filleted by hand and the fillets were rinsed briefly, drained on an inclined screen for 5 min, and weighed. Notes were made on the appearance of the round fish and the condition of the gills, fillets, and viscera. The fillets were then ground using the coarse blade on an Oster² food grinder. A composite of 800 g was frozen at -34° C. The remaining

ground flesh was washed with cold water (1 flesh:2 water) for 15 min on a reciprocating shaker. The flesh was drained for 30 min on an inclined 16-mesh plastic screen, then weighed and frozen at -34° C for later analysis. All analyses were completed within 2 mo and we assumed no changes took place during frozen storage.

Formal Sensory Evaluation

Pollock (Lot 2) were separated from the rest of the catch and stored on the deck of the boat. The fish were frequently sprayed with fresh seawater to keep them cool. About 6 h after capture, the fish were transferred into the ice and MRSW holding systems. A control sample was taken at this time. The icing was less thorough than in Lot 1. Temperature and pH of the MRSW holding system were maintained at the same values as in Lot 1. At regular intervals, fish were removed from each holding system and filleted by hand. About 7 kg of fillets were frozen as blocks in plastic bags at -34° C for formal sensory evaluation. The remaining fillets were ground and stored at -34° C for later chemical analysis. Chemical and sensory analyses were completed within 2 mo. The last sample (12 days) was not large enough for the taste panel test and was evaluated by chemical methods only.

The blocks were sawed into portions measuring 80 × 50 × 12 mm and thawed at room temperature. The control sample and samples from fish held in ice were salted by immersion in a 5% NaCl solution for 1.5 min. The portions were cooked in individual sealed aluminum pans at 232° C for 20 min in a commercial oven. Because of the difficulty in equalizing the salt content, samples from the two holding systems were not directly compared. Judges were asked to note if a sample were too salty. The results of the sensory tests were evaluated by analysis of variance. If analysis of variance indicated a change had occurred with time of holding, the Student-Newman-Keuls test was used to determine which samples were different.

Chemical Analyses

The frozen samples were tempered overnight in a refrigerator at 3° C and ground twice using the fine blade of an Oster food grinder. Analyses were carried out for total nitrogen, total solids, chloride (Horwitz 1975), total volatile acid (TVA,

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

Friedemann and Brook 1938), total volatile base (TVB, Stansby et al. 1944), and extractable protein nitrogen (EPN, Dyer et al. 1950). Analyses for formaldehyde (FA, Castell and Smith 1973), trimethylamine oxide (TMAO, Bystedt et al. 1959), free α -amino-nitrogen (Pope and Stevens 1939), and nonprotein nitrogen (NPN, Nikkilä and Linko 1954) were carried out on a 5% trichloroacetic acid extract. An aliquot of the extract was neutralized and analyzed for dimethylamine (DMA) by Dowden's (1938) method modified by increasing the time of extraction to 15 min and by using a mechanical shaker. Analysis for trimethylamine (TMA) in fish in Lot 1 was carried out using Dyer's original method (Dyer 1945). For fish in Lot 2, Dyer's method and the modification by Tozawa et al. (1971) were used.

RESULTS AND DISCUSSION

Physical Appearance and Yield

Changes in odor, degree of decomposition of viscera, and physical appearance of fish from Lot 1 and Lot 2 occurred at the same time of holding. Ice-held fish were generally free of slime whereas fish held in MRSW were covered with a thin layer of slime throughout the experiment. After a few days, the gills and fins of fish held in ice were firm but those in MRSW were soft and swollen. After 4 days in ice, the pollock had soft livers and after 6 days, decomposition of the viscera could be detected externally. Softening of fillets became noticeable in 2 or 3 days in fish from both holding systems. An unpleasant odor became noticeable after 3 days in ice and predominant after 4 days. Browning of the fillets appeared after 6 days in ice and seemed to be

enhanced by grinding. Based on this informal subjective observation on the physical appearance and odor of the fish in the round and the raw fillet, pollock could be held a maximum of 4 days under ideal icing conditions before becoming unacceptable for human consumption.

Pollock held in MRSW showed the same changes as those held in ice but they occurred several days later. The maximum time the fish could be held in MRSW and still be acceptable for consumption was 8 days based on evaluation of the fish in the round and the raw fillets. The amine odor usually associated with deterioration of fish was not present but there was a distinct and unpleasant smell in the fillets of fish held more than 12 days in MRSW. The changes in odor and texture occurred gradually in fish from either system, so the exact time for onset of spoilage based on these informal, subjective evaluations could not be reliably determined.

Pollock held in either medium gained weight steadily throughout the experiment (Table 1). The increase was more than 6% of the initial weight after 5 days in MRSW but only 3% in ice. The yield of fillets averaged 36% in both media and remained fairly constant. Solids content of the flesh decreased from 18% initially to 16% and 17% after 10.5 days in ice and in MRSW, respectively (Table 1). Solids contents of fish in Lot 2 were similar. The higher solids content of fish held in MRSW was probably caused by the uptake of salt (Table 1).

Sensory Assessments

Differences in odor and firmness were highly noticeable in raw fillets from fish held different lengths of time in the same holding system or

TABLE 1.—Change in weight, salt, and total solids content of fillets and washed ground flesh of walleye pollock (Lot 1) with time of holding in ice and in modified refrigerated seawater.

Time (days)	Ice holding system									Modified refrigerated seawater								
	Round weight ¹		Fillets			Washed ground fillets			Round weight ¹		Fillets			Washed ground fillets				
	Initial (g)	Final (g)	Weight (g)	NaCl (%)	Solids (%)	Weight ² (g)	NaCl (%)	Solids (%)	Initial (g)	Final (g)	Weight (g)	NaCl (%)	Solids (%)	Weight ² (g)	NaCl (%)	Solids (%)		
0	6,383	6,383	2,268	0.13	18.2	2,661	0.07	12.3	6,383	6,383	2,268	0.13	18.2	2,661	0.07	12.3		
0.5	6,616	6,615	2,356	0.14	18.0	2,384	0.05	12.5	—	—	—	—	—	—	—	—		
1.5	6,299	6,324	2,333	0.13	17.6	2,718	0.05	12.6	7,456	7,656	2,541	0.58	19.1	2,730	0.23	14.5		
2.5	6,433	6,520	2,262	0.14	17.5	2,487	0.07	13.0	6,910	7,244	2,618	0.76	18.5	2,695	0.29	14.8		
3.5	6,180	6,271	2,331	0.14	17.1	2,637	0.05	12.9	7,038	7,386	2,642	0.94	18.3	2,685	0.38	15.2		
4.5	6,428	6,583	2,483	0.14	17.4	2,947	0.05	12.4	6,835	7,270	2,571	1.07	18.4	2,550	0.42	15.7		
6.5	6,630	6,816	2,510	0.15	16.8	2,837	0.04	12.6	7,264	7,882	2,828	1.21	18.0	2,773	0.46	15.0		
8.5	6,372	6,713	2,376	0.11	16.6	2,685	0.04	12.4	7,352	8,022	2,872	1.34	17.9	2,805	0.58	15.2		
10.5	6,674	6,986	2,441	0.10	16.4	2,799	0.05	12.4	7,017	7,777	2,591	1.55	17.5	2,473	0.66	15.7		
12.5	—	—	—	—	—	—	—	—	6,845	7,755	2,535	1.64	17.6	2,395	0.64	15.2		
13.5	—	—	—	—	—	—	—	—	7,096	8,003	2,715	1.64	17.4	2,578	0.69	15.3		
15.5	—	—	—	—	—	—	—	—	6,750	7,727	2,597	1.69	17.1	2,497	0.70	14.8		

¹Total round weight of the fish that composed the sample.

²Weight of ground, washed flesh if no portion had been reserved for analysis of fillets.

equal lengths of time in different holding systems, but were almost absent in the cooked samples (Table 2). The flavor scores of iced pollock did not change significantly until after 6 days and texture remained unchanged throughout the experiment. Kramer et al. (1977) reported that pollock can be held 12 days in ice with only a small decrease in flavor scores and none in texture scores. The pollock used in that experiment were larger than those used in our work, and preparation and cooking of the fish were different.

The flavor scores for the MRSW samples remained unchanged to 4 days and were acceptable to 8 days except for the high salt content. The increased salt content, in addition to the development of a disagreeable taste noted by some panel members, was probably the reason sensory scores decreased after 4 days in MRSW. The scores for texture remained unchanged throughout the experiment.

These conclusions on holding characteristics of pollock were based on fish obtained from one location at one time of year but pollock caught at different locations may have different holding properties (Kramer et al. 1977). Not only does the size of walleye pollock vary from one location to the next (Kizevetter 1973) but there is some evidence of distinct breeding groups (Iwata 1975). Variation due to the yearly reproduction cycle may also affect the holding qualities.

Chemical Analyses

While the salt content of pollock held in ice remained relatively unchanged with time of holding, it increased rapidly in MRSW-held fish (Table 1). Salt contents of fish from both lots were similar. The protein contents ($6.25 \times \% \text{ total N}$) of the fillets varied little with holding time and averaged

TABLE 2.—Change in mean sensory analysis scores for baked portions of blocks of fillets of walleye pollock (Lot 2) with time of holding in ice and in modified refrigerated seawater (MRSW). SD are in parentheses. Panel had 12 judges. Flavor and texture scores were on the following scale: Very good, 5; Good, 4; Fair, 3; Borderline, 2; and Poor, 1.

Time of holding (days)	Flavor		Texture		Percent responding too salty	
	Ice ¹	MRSW ¹	Ice	MRSW	Ice	MRSW
0	4.0 (0.5)	4.0 (0.5)	4.0 (0.3)	4.0 (0.7)	0	0
2	3.9 (0.5)	3.7 (0.5)	3.9 (0.5)	3.9 (0.5)	0	0
4	3.6 (0.5)	4.1 (0.5)	3.8 (0.5)	4.0 (0.7)	0	0
6	3.8 (0.6)	2.9*(0.9)	3.8 (0.6)	3.9 (0.7)	0	33
8	3.2*(0.8)	3.2*(0.7)	3.8 (0.5)	3.8 (0.4)	0	75

¹Values with asterisk were significantly ($P < 0.05$) different from zero holding time values.

16.5% in either system for both lots. The nonprotein nitrogen content was 11% of the total nitrogen content initially and did not change with time of holding in ice but slowly decreased to 7% after 10 days in MRSW. The free α -amino-nitrogen content did not change significantly during the experiment, averaging 7.1 ± 0.7 (SD) and 6.2 ± 0.9 (SD) mg N/100 g sample in the fillets of fish held in ice and in MRSW, respectively.

Several chemical analyses were performed to determine which, if any, could be used as an index of spoilage. TVB changed little and never exceeded 10 mg N/100 g sample making it unsuitable as an index of spoilage. Tokunaga (1964) reported TVB values of 10-13 mg N/100 g sample for freshly caught pollock. Analysis for TVA in fish from Lot 2 gave values essentially the same as in Lot 1. Except for the 2.5-day sample, values for TVA content of ice-held fish remained largely unchanged at $< 0.20 \text{ meq H}^+ / 100 \text{ g flesh}$ to 4.5 days but then began to increase (Figure 1). The increase at 4 days coincided with the change in quality as determined by informal subjective evaluation of the raw fillets but preceded by at least 2 days the decrease in flavor scores of the cooked fillets. Therefore, TVA content could be used as an index of spoilage for pollock held in ice if supplemented by subjective sensory examination of cooked fish. For MRSW-held samples, a rapid increase in TVA content occurred after 12 days while a significant

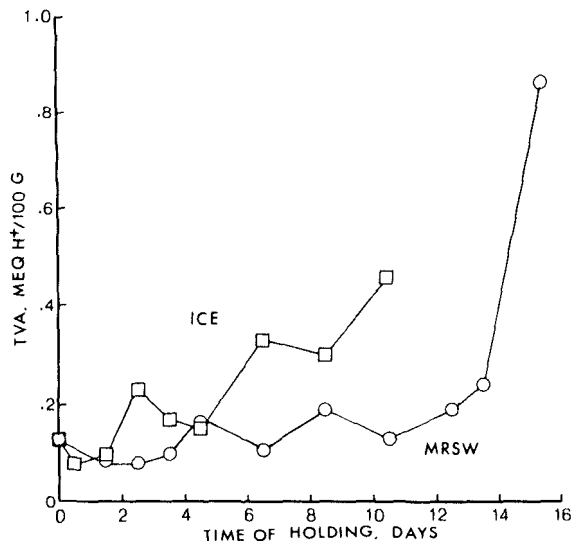


FIGURE 1.—Change in total volatile acid (TVA) content of fillets from walleye pollock (Lot 1) with time of holding in ice and in modified refrigerated seawater (MRSW).

decrease in quality was detected at 8 days in the raw fillets, and at 6 days in the cooked fish. Therefore, TVA could not be used as an index of spoilage for pollock held in MRSW.

In both lots, the TMA values (Dyer 1945) were higher for ice-held fish than for MRSW-held fish (Figure 2). A higher TMA content should have occurred in the fish held in ice if their flesh was at a higher pH because Castell and Snow (1949) showed the rate of formation was higher in a more basic medium. The pH of a 2:1 distilled water-ground flesh mixture was 7.25 and 6.45 for ice-held and MRSW-held fish, respectively, and changed little with time of holding. Another reason for the higher TMA content in iced fish was that the lower pH of the brine should inhibit the proliferation of bacteria. For fish held in MRSW, there was little difference in TMA content between lots but for fish held in ice, values for Lot 2 are about twice the corresponding values in Lot 1. This difference in TMA values between lots was probably due to the fish in Lot 2 being iced in

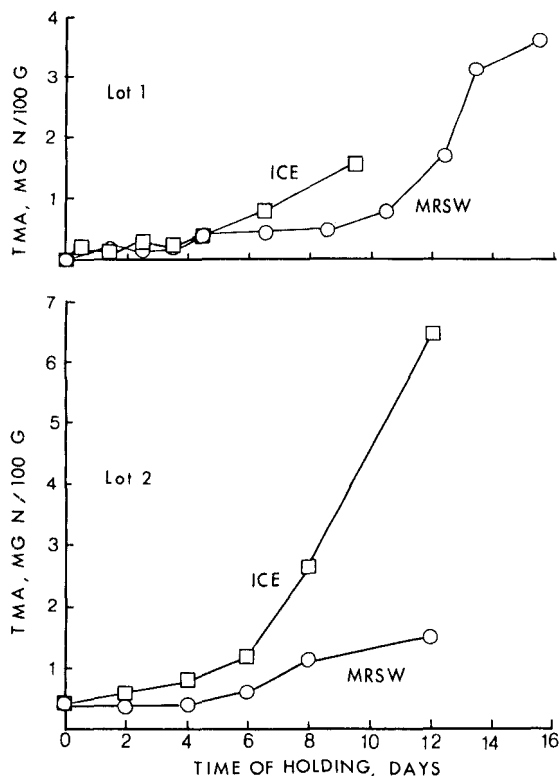


FIGURE 2.—Change in trimethylamine (TMA) content of fillets from walleye pollock with time of holding in ice and in modified refrigerated seawater (MRSW).

layers while those in Lot 1 were individually iced. Kramer et al. (1977) reported TMA values on iced pollock that were similar to that of Lot 1. Although there was no statistically significant correlation between flavor of iced fish and TMA content, the rapid change in TMA content for iced fish from Lot 2 occurred at the same time as the flavor score decreased. The change in rate of accumulation of TMA in iced fish in Lot 1 was not as discernible but probably occurred between 4 and 6 days. Kramer et al. (1977) reported a large increase in TMA content in pollock after 8 days in ice. Differences in analytical technique, sample preparation, or icing procedure could account for the different times for the sudden increase in TMA. For MRSW-held fish in Lot 2, no rapid change in TMA content was noted even after the flavor scores decreased. Consequently, TMA content may provide a useful index of spoilage for ice-held pollock but may not be useful for fish held in MRSW.

Using the modification by Tozawa et al. (1971) of Dyer's (1945) method for determining TMA has reduced the interference from DMA but has not always provided as reasonable or as useful data (Botta and Shaw 1975; Shaw et al. 1977). Fish from Lot 2 were analyzed by both methods and though TMA values were generally lower using the method of Tozawa et al., there was no difference in the way TMA content varied with time of holding. Consequently, the methods of Dyer and Tozawa et al. were equally useful as chemical indices of spoilage for pollock during fresh storage in ice. The TMA values as determined by the method of Tozawa et al. were not included in this report.

The TMAO content (Lot 2) of the zero holding time sample was 69 mg N/100 g flesh. Tokunaga (1964) has reported TMAO values which averaged about 100 mg N/100 g flesh. The TMAO content of the ice-held fish remained essentially unchanged to 8 days but dropped to 36 mg N/100 g flesh on the last day (Figure 3). The TMAO content of fish held in MRSW was about the same as that of fish held in ice to the fourth day then rapidly decreased. Although there was no significant statistical correlation between TMAO values and flavor scores, the decrease in TMAO content coincided with the decrease in flavor scores for MRSW-held fish. The TMAO content of the ice-held fish had not changed significantly at the eighth day of holding even though the flavor score had decreased significantly.

The DMA content was also determined on fish in Lot 2 (Figure 4). The rate of accumulation of DMA

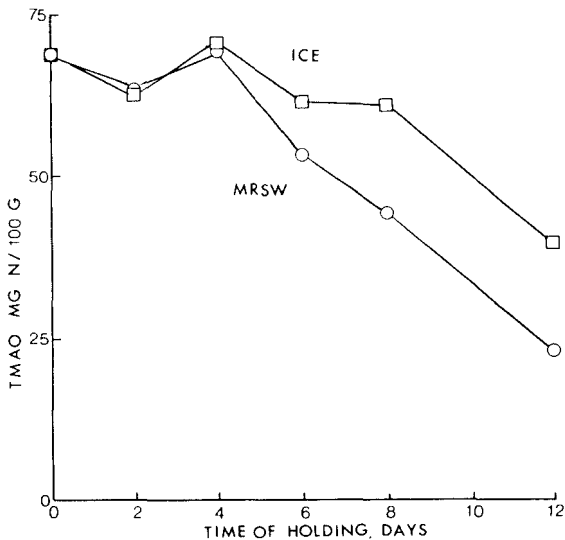


FIGURE 3.—Change in trimethylamine oxide (TMAO) content of fillets from walleye pollock (Lot 2) with time of holding in ice and in modified refrigerated seawater (MRSW).

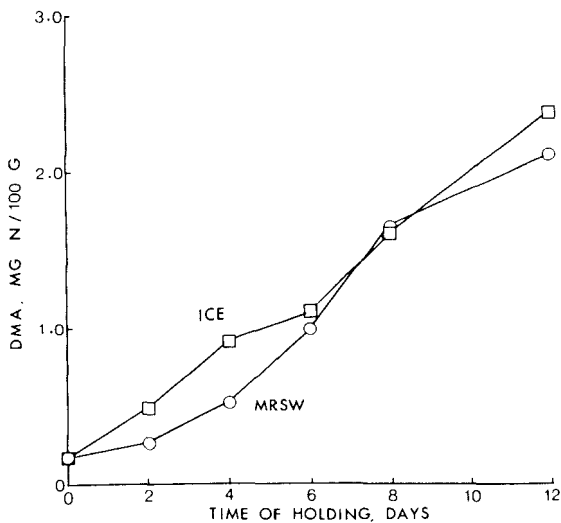


FIGURE 4.—Change in dimethylamine (DMA) content of fillets from walleye pollock (Lot 2) with time of holding in ice and in modified refrigerated seawater (MRSW).

was linear and equal in both systems and therefore had little usefulness as an index of spoilage. Because of the leaching ability of both the melt water in the ice system and the brine in the MRSW system, the rate of accumulation of DMA in the flesh may be different from the rate of formation of DMA. In the dissociation of TMAO, FA should be

formed in equal molar proportion to DMA. The results for analysis for FA in fish from Lot 2 revealed that FA content was 4 ppm in both systems and did not change with time of holding. The lack of an increase in FA content was probably due to its reaction with proteins. Castell et al. (1973) noted that addition of FA lowered the solubility of the protein so the formation of FA can be inferred by a decrease in EPN with time of holding (Figure 5).

Results from an experiment on a control sample to which NaCl was added indicated that the low EPN values of MRSW-held fish were not due to their high salt content. Like the TMAO content, the values for EPN are about the same for either holding system until after 4 days when the values for MRSW-held fish decreased rapidly (Figure 5). Data from fish in Lot 1 also indicated that there was a similar difference in solubility after 4 days of holding. Although there was no significant statistical correlation among EPN values, TMAO content, or the flavor scores, all three of these experimentally determined values decreased at the same time in fish held in MRSW, i.e., after 4 days. With ice-held fish, the decrease in flavor preceded the decrease in TMAO and there was no decrease in EPN values. Evidently, analysis for TMAO and EPN may provide an index of spoilage for MRSW-held fish but not for ice-held fish. Tokunaga (1964) reported data similar to that

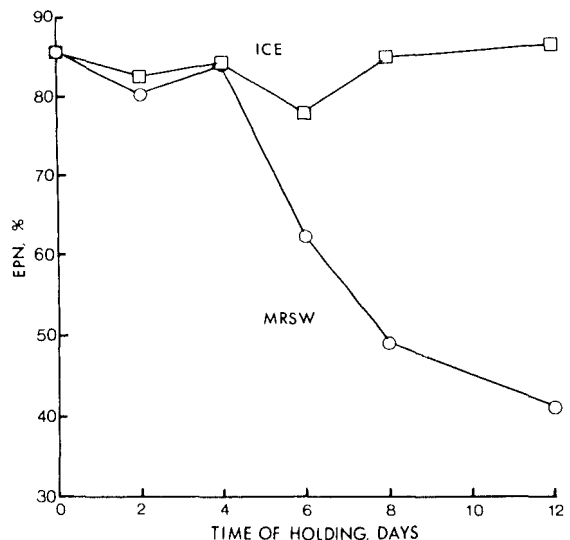


FIGURE 5.—Change in extractable protein nitrogen (EPN) of fillets from walleye pollock (Lot 2) with time of holding in ice and in modified refrigerated seawater (MRSW).

presented here on the accumulation of DMA and FA in the flesh of walleye pollock stored as fillets at 1°-3° C. Kramer et al. (1977) reported much lower values of DMA but this was probably due to differences in sampling and analytical technique.

Effects of Washing Ground Flesh

Washing improved the appearance of minced pollock (Miyachi et al. 1977) and is a common procedure in the utilization of pollock in traditional Japanese products (Okada and Noguchi 1974). The water to flesh ratio of 2:1 used in this experiment was much smaller than the 5:1 or larger values used by other investigators. Washing the ground flesh of ice-held pollock increased the apparent yield but no change in yield occurred for samples held in MRSW. If yield data are converted to a salt-free, constant 18% solids basis however, the washing procedure actually decreased the yield to 30% for samples from either system. Yamamoto et al. (1975) reported that 20% of the protein content of ground pollock can be lost under certain washing conditions. Consequently, for commercial purposes, any beneficial results from washing would have to be balanced against a sizable decrease in yield. The advantages of washing are that the product is lighter in color, has less odor, and, in the case of fish held over 4 days in MRSW, has an acceptable salt content (Table 1). TMA, TVA, and NPN content are also reduced by about half on washing.

CONCLUSIONS

Walleye pollock can be held to 6 days if iced thoroughly and still be acceptable for human consumption. Palatable fillets can be obtained from ice-held fish whose physical appearance in the round would probably cause them to be rejected for human consumption. In MRSW, the rapid accumulation of salt in the flesh would prohibit holding pollock more than 4 or 5 days at the 1.5:1 brine to fish ratio utilized in this experiment. The development of a disagreeable taste other than saltiness may be responsible for some of the decrease in flavor scores. The beneficial results of washing the ground or minced flesh of pollock will probably be negated by the decrease in yield and the problems associated with disposing of the wash water. Analysis for TMA or TVA may provide a chemical index of spoilage for pollock held in ice; for pollock held in MRSW, analysis for TMAO or EPN may be

useful. Further work is needed before limiting values for TVA, TMA, TMAO, or EPN can be proposed as objective indicators of the acceptability of fresh pollock.

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