Utilization of Red Hake

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It has been estimated that the optimal yield of red hake, *Urophycis chuss* (also called squirrel hake, mud hake, and ling), is 32,000 metric tons (t). This is an increase from the 1978 optimal yield estimate which was 16,000 t. The international catch of this fish from Georges Bank in 1977 was 2,879 t with the U.S. commercial catch being just 96 t. Thus, there is an abundant resource of this species for development.

At present the utilization of red hake in the United States is minor with just a limited market for fresh fillets or whole fish. This species has an excellent, mild flavor with a slightly soft texture which progressively deteriorates during storage at refrigerator temperatures above freezing. In the United States, red hake is usually not marketed in any form other than fresh.

Seafood processors are constantly searching for new resources that would open new markets. One opportunity for this would be the expansion of the red hake fishery and subsequent development of a domestic fish block manufactory. A major deterrent to the development of a market for frozen red hake is the relatively short storage life of this species at commercial freezer temperatures due to the development of a tough, spongy, rubbery texture (Dyer and Hiltz, 1974).

Textural changes during frozen storage of fish can be due to several causes. Among these are denaturation of fish proteins brought on by free fatty acids released during frozen storage (Anderson and Ravesi, 1970) or by cross-linking of proteins brought about by compounds produced during oxidative breakdown of fish lipids. Red hake, however, contains a relatively low proportion of fat (approximately 0.8 percent, wet weight basis), and the rate of oxidation of this fat in frozen storage is very slow.

As is typical for the gadoid species, red hake are subject to a further type of change, i.e., the conversion of trimethylamine oxide to dimethylamine and formaldehyde which presumably occurs by an enzyme-catalyzed reaction (although it is known that under some conditions this breakdown of trimethylamine oxide can occur nonenzymatically catalyzed, e.g., by Fe^{+2} (Castell, 1971)). One of the breakdown products of trimethylamine oxide, formaldehyde, is an effective cross-linking reagent capable of interacting with two molecules of protein. It is probable that such cross-linking is the principal cause of toughening of texture in frozen storage.

Trimethylamine oxide is ubiquitously found in the muscle of marine fish. The uniqueness of the red hake muscle may lie in its capability to rapidly convert its trimethylamine oxide to dimethylamine and formaldehyde. It has, in fact, been shown (Dingle et al., 1977) that the minced flesh of red hake will greatly accelerate trimethylamine oxide breakdown in a nongadoid fish. It has been reported that the dark muscle of gadoid fish contains higher concentrations of trimethylamine oxide and its breakdown products than does light muscle (Simidu, 1961). Preliminary results in the University of Massachusetts Marine Foods Laboratory indicate that the total concentration of trimethylamine oxide and its breakdown products is approximately the same in the light and dark muscle. However, under similar storage conditions there are more breakdown products formed in the dark muscle indicating that the system (presumably enzymatic) for breaking down trimethylamine oxide is more active in the red muscle. Any contamination by kidney or blood during production of the fish fillet or the minced flesh would also give an increased rate of breakdown of trimethylamine oxide.

Mincing is known to increase the rate of dimethylamine production (Hiltz et al., 1976) which is a common measure of trimethylamine oxide breakdown. It has been suggested (Dingle and Hines, 1975) that minced flesh may be washed to remove trimethylamine oxide and prevent the formation of dimethylamine and formaldehyde. Such a process may be useful in the production of surimi for export to foreign markets, particularly Japan.

With Pacific whiting it has been

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found that the exclusion of oxygen did not retard the formation of dimethylamine or formaldehyde during frozen storage (Babbitt et al., 1972). In the same report, it was also found that the type of package had little effect on the breakdown.

Several excellent studies have been carried out on the rate of conversion of trimethylamine oxide to dimethylamine and formaldehyde in frozen gadoid muscle (Babbitt et al., 1972; Castell et al., 1973; Tokunaga, 1974; Dingle et al., 1977). These studies have generally measured formation of dimethylamine and formaldehyde and a loss in extractable protein nitrogen. A recent study (Gill et al., 1979) has related chemical and physical measurements to sensory perceptions of toughness in frozen red hake muscle at −5° and −17°C over a period of 39 days. It has been estimated that the frozen storage shelf life for hake at −4°F is 22 weeks (Dyer and Hiltz, 1974). This estimate was based on a prediction of loss of protein solubility (extractable protein nitrogen).

The Marine Foods Laboratory at the University of Massachusetts Marine Station, Gloucester, currently has studies underway sponsored by the New England Fisheries Development Program to define the shelf life of frozen fillet blocks of red hake under commercial storage conditions (0°F). The study will include samples which have been saberized (deep-skinned) to remove some of the red muscle, as well as the use of 1-day old and 5-day old fish to determine the effect of postmortem age on textural development. We are also beginning research in conjunction with the National Marine Fisheries Service, Gloucester Laboratory, and Cornell University on preventing the decomposition of trimethylamine oxide to dimethylamine and formaldehyde and/or preventing further reaction of formaldehyde that is formed with protein or other components leading to large macromolecular aggregates responsible for the undesirable texture.

There are three general approaches that may be taken to achieve the goals. First, we can prevent the decomposition of trimethylamine oxide; thus, no formaldehyde would be formed. Second, we can prevent the formaldehyde which does form from interacting with those components leading to a toughening of texture. Third, reaction of formaldehyde with the protein could possibly be reversed although we feel that this last approach holds the least chance for success.

To prevent formaldehyde from being formed several approaches may be taken. One of these would be to remove the trimethylamine oxide by a washing procedure. This would be simpler in the case of minced flesh since diffusion will be a problem in the intact muscle. However, there may be ways of improving penetration of the washing solution. The enzyme converting the trimethylamine oxide to dimethylamine and formaldehyde may be inhibited or deactivated. A major approach will be to look at potential enzyme inhibitors which are also acceptable food additives for this purpose. Heating of the tissue before freezing may also be accomplished. It may be desirable to freeze a product in the raw form for a given length of time and then heat it at a later time as the product is processed into a final consumer product.

Modification of the pH of the flesh may affect either the reaction of formaldehyde with component proteins or make the enzyme-catalyzed reaction less favorable. Removal of the part of the fillet which is particularly rich in red muscle may also remove a disproportionally greater amount of enzyme, thus slowing the reaction. This may be accomplished by saberizing as discussed above or perhaps by removing a relatively small proportion of the total fillet (7 to 8 percent) near the tail portion which is particularly rich in dark muscle.

Formaldehyde may be prevented from reacting with the components which lead to toughening by: 1) removing formaldehyde by a procedure such as washing; 2) by causing it to react with components which do lead to changes in texture (these may be native components or components added to the tissue, such as compounds containing free amino groups); 3) by controlling environmental factors like pH to make conditions less favorable for the reaction to occur; 4) by converting formaldehyde into a different compound which does not cross-link protein; and 5) possibly by controlling the location of the macromolecules so that even though formaldehyde reacts with them, it cannot react with more than one thus preventing cross-bridge formation. This would be done by the rate of freezing and the control of ice crystal growth. When ice crystals are allowed to form slowly, they form in the extracellular space and compact the protein molecules making them presumably easier to cross-link. If freezing is very rapid the proteins may remain spatially separated and less likely to cross-link with other protein molecules.

A major effort will be made on the effect of preprocessing conditions on the response of the muscle tissue to changes during frozen storage. The manner of holding the fish on board the vessel, e.g., icing vs refrigerated sea-water storage, will be examined. Also it is expected that postmortem age of the red hake may be a significant factor. Since there is some softening with refrigerated storage, this may somewhat counterbalance the toughening which occurs during long-term frozen storage.

A related problem which has to be considered is how much of the reaction between the protein and formaldehyde occurs during frozen storage and how much occurs during the heat processing necessary to make the fish "table ready." Some preliminary results at the University of Massachusetts have indicated that up to 50 percent of the reaction of formaldehyde in the tissue occurs during the cooking process itself. However, this proportion is expected to vary greatly and be dependent on several factors, including the amount of formaldehyde and the exact processing procedures.

The economic value of fresh fish is significantly higher in many cases than that of frozen fish. Thus, if an underutilized fish such as red hake could be moved in the fresh form, it

may better be able to compete favorably with the higher priced species currently available to the U.S. consumer. If, in addition, the shelf-life could be extended, new markets would open up, both further inland within the United States and, of course, around the world. In the inland American market we would be introducing this low fat white-fleshed fish to an audience that is not already strongly committed to one of the more common coastal species; in the international market, we would be dealing with a consumer audience that accepts a much broader range of quality fish products.

With red hake, we are also specifically concerned with the textural changes that occur in the frozen product as were discussed elsewhere in this paper. Thus, by handling red hake in the fresh form some of these problems may be avoided. Furthermore, in those cases where the fish will be further processed, it may be more efficient in terms of labor, energy, and product quality to process red hake directly from the fresh form.

Preliminary results suggest that once the product is cooked, and the enzyme causing the undesirable textural change is destroyed, red hake can be stored frozen far more successfully than when it is frozen raw. Particularly in the case of minced flesh obtained either from whole fish or from bone racks after filleting, immediate heating after processing may lead to a more desirable product. It may also be helpful to be able to store red hake safely in the fresh form until it can be processed, especially when an excess has been landed. Thus there are many reasons for the interest in extending the shelf life of red hake for which a number of different approaches might be taken. At Cornell University, we are pursuing the following approaches (with Sea Grant support):

1) The addition of an antibacterial chemical to the ice may slow down the growth of surface bacteria. Since this is the major route of spoilage of fresh fish, particularly the production of trimethylamine by *Pseudomonas putrefaciens*, the inhibition of this bacterial spoilage should extend the shelf life of the fish. Clearly, the additive used must be an approved food additive.

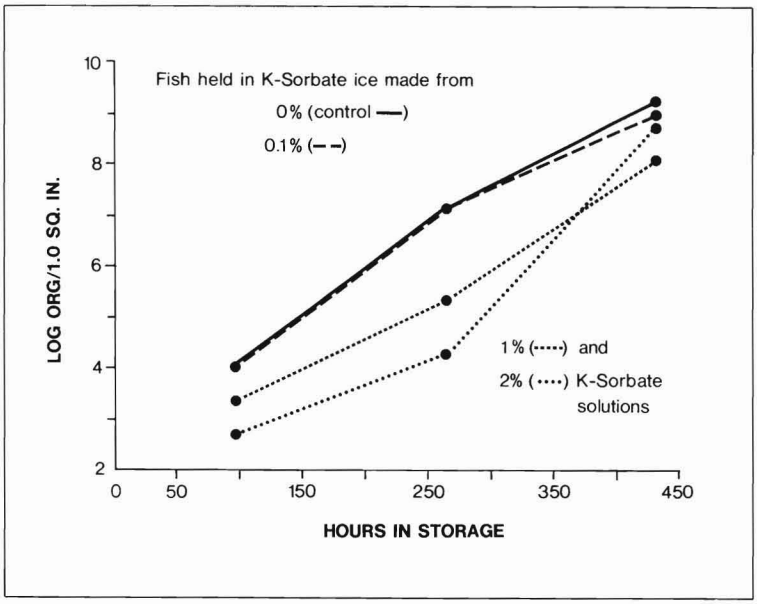


Figure 1.—Log psychrotroph count of potassium-sorbate ice treated fish with respect to time in storage. Fish were held in potassium-sorbate ice made from 0 (control), 0.1, 1, and 2% weight/volume potassium-sorbate solutions.

One compound that is currently under investigation for use in a number of flesh foods is the recently reviewed compound, potassium sorbate. It is generally recognized as safe (a GRAS compound); is antimycotic, and inhibits the outgrowth of *Clostridium botulinum* spores.

The U.S. Department of Agriculture is proposing to add 0.26 percent of this compound directly to bacon to replace some of the nitrite currently being used. It has also been proposed for use in ship-board refrigerated seawater systems, particularly with salmon. With funds from the Monsanto Company[1], we have investigated the effect of potassium sorbate on a number of properties of red hake.

A short-time dip (approximately 1 minute) was relatively ineffective, even when up to a 5 percent potassium sorbate solution was used. However, it clearly inhibited the bacterial population when used in the cooling ice at 1 and 2 percent levels.

Figure 1 shows the psychrotrophic bacterial count of a surface swab which was measured at 7°C for 10 days. We also measured a number of other properties, in particular the TMA (trimethylamine) values, and various organoleptic (taste panel) properties. All the results suggested a shelf life extension of a few days.

As part of this series of experiments, we have also been examining the use of the Torry meter as a rapid way to measure quality. This meter measures changes in electrical properties of the fish from a high of 16 to a low of 0. (A previously frozen fish gives a reading of 3 or below.)

The use of such a meter, if it works, would be most beneficial with less familiar species of fish. This instrument did indicate different values for the treated and untreated samples (Fig. 2) and the values decreased as spoilage progressed. Overall sensory acceptability of cooked fish as a function of time

[1]Reference to trade names or commercial firms does not imply endorsement by the National Marine Fisheries Service, NOAA.

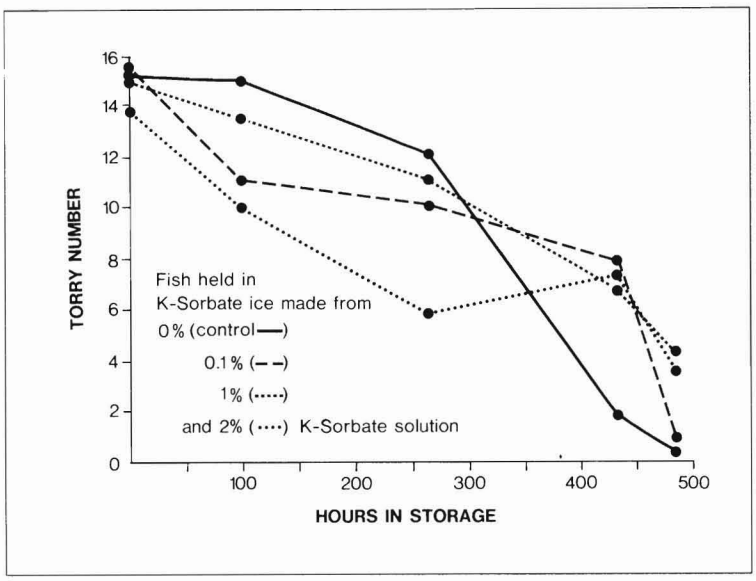
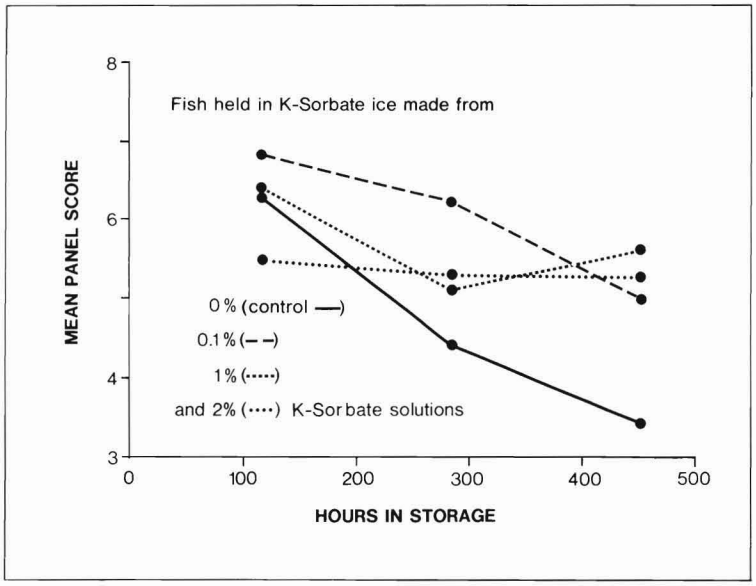


Figure 2.—Torrymeter numbers of potassium-sorbate ice treated fish with respect to time in storage. Fish were held in potassium-sorbate ice made from 0 (control), 0.1, 1, and 2% weight/volume potassium-sorbate solutions.

Figure 3.—Organoleptic evaluation: mean panel scores for overall acceptability in potassium-sorbate ice treated fish with respect to time in storage. Fish were held in potassium-sorbate ice made from 0 (control), 0.1, 1, and 2% weight/volume potassium-sorbate solutions.



on sorbate-containing ice is given in Figure 3.

Another property of the red hake which we examined was the thiobarbituric acid values (TBA). This test is used to measure the development of fat rancidity in foods. Our results suggested that very little change was occuring in the small amounts (less than 1 percent) of fat present in red hake, and we have thereafter discontinued making these measurements.

2) The second phase of the research was to examine the effects of modified atmospheres. Particularly in transportation systems, it is possible to charge a refrigerated van with various gases; however, it is generally left alone thereafter and is thus subjected to natural changes. (In controlled atmosphere systems, more elaborate controls monitor the condition of the gases and maintain a constant pre-set level.)

Modified atmospheres have been particularly effective with beef and plant commodities and thus the necessary reefer (refrigerated) vans for this type of shipping already exist. Sea-Land Services, a transoceanic container ship company, has helped to sponsor this aspect of the research.

To test a number of different atmospheres economically in a limited amount of space, we have designed a system centered around barrier bags (supplied by the Cryovac division of W. R. Grace, Inc.). Individual fish were placed in these bags without ice. A septum using silicon glue was attached to each bag so that the bags could then be inflated with various mixtures. The gases could also be extracted in small quantities at various times in order to analyze changes by gas chromatography. The system of individual bags also allowed us to remove entire samples of fish as we needed them without disturbing the other samples.

These experiments clearly showed the advantage of high (20 and 60 percent) carbon dioxide (CO_2) atmospheres. The addition of carbon monoxide did not have any positive effect at the 1 percent level. It should be pointed out that the fish were stored at about 0°−1°C, a temperature range that

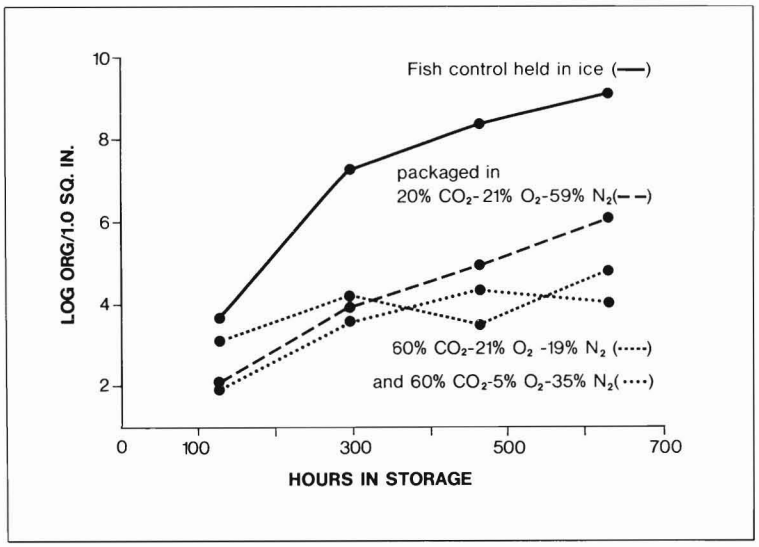
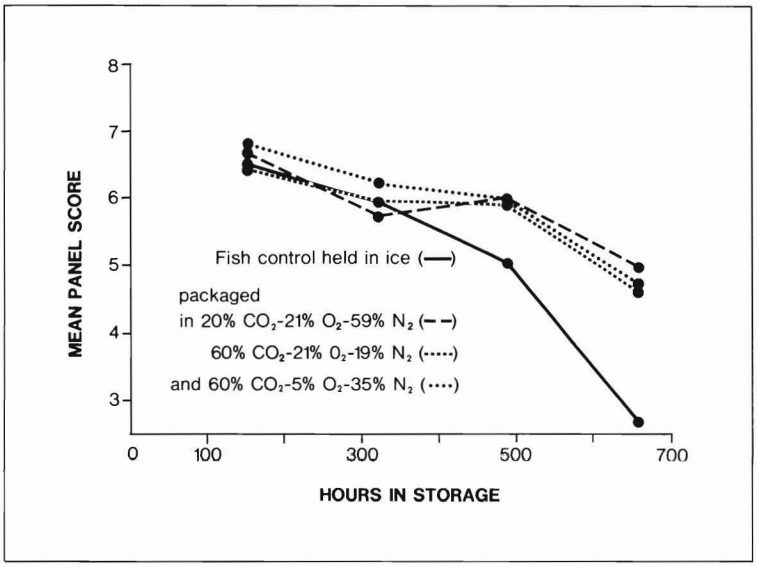


Figure 4.—Log psychrotroph plate count of fish held in ice and fish packaged in modified atmospheres with respect to time in storage. Fish were held in ice (control), packaged in 20% CO_2-21% O_2-59% N_2, 60% CO_2-21% O_2-19% N_2, and 60% CO_2-5% O_2-35% N_2.

Figure 5.—Organoleptic evaluation: Mean panel scores for overall acceptability of fish held in ice and fish packaged in modified atmospheres with respect to time in storage. Fish control held in ice (control), packaged in 20% CO_2-21% O_2-59% N_2, 60% CO_2-21% O_2-19% N_2, and 60% CO_2-5% O_2-35% N_2.



is routinely used in commercial refrigeration. Figures 4 and 5 show some of the results obtained with CO_2; significant shelf life extension of the red hake was obtained.

One side effect noticed in this phase of the work was that the bags retained any off-odors formed. We have called this the "bag-effect." In order to minimize this effect, which would also be present in commercial systems, we have tried to develop an air scrubbing system. We have found that bubbling the air through sulfuric acid in a closed system will lead to the formation of a trimethylamine sulfate precipitate and we are hopeful that this will decrease the internal odor, eliminating the "bag-effect."

3) In the last phase of this series of experiments, we are using larger bags in which the fish are placed in a container with a raised screened bottom which permits the melting water to drip away from the fish. This allows us to use both gas and ice (with and without potassium sorbate) to test the possible synergistic effects of the two systems. The gas scrubbing system has also been included. Using this system we cannot remove samples of fish at intermediate times; thus only the condition of the fish at the end of an arbitrary storage period can be determined.

Another area that we hope to pursue in the future is the use of a coating, such as an alginate glaze. This would protect fish against moisture loss in long-term refrigerated storage and could be used to hold the potassium sorbate. (Presumably with continuous contact, the amount of sorbate needed would be much less.)

In conjunction with Sea-Land Services, which has recently built a mobile lab within a shipable container, we hope to test some of our ideas on an actual shipment of fish. We are extremely optimistic that this and related research will lead to a further exploitation of the red hake resources of the northwest Atlantic.

Acknowledgments

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