

## CHEMICAL CHANGES IN FISH PROTEIN DURING FREEZING AND STORAGE

It is a well known fact that a decided consumer preference for fresh fish to frozen fish exists in many areas, despite the convenience of the frozen product. The reasons for this preference have been well recognized and have been the basis for extensive study throughout the world for many years.

The important changes in fishery products that have been associated with freezing and cold storage are the loss of tenderness and characteristic fresh-fish flavor, with subsequent development of toughness, off-flavors, and off-odors. The development of off-flavors and off-odors is usually caused by fat oxidation, even in lean fish such as cod and haddock. The loss of characteristic fresh-fish texture has been related to what is called protein denaturation, or, more simply, alteration, and it is this problem that is currently receiving the attention of several laboratories, including the Fishery Products Laboratory (Ketchikan, Alaska).

Proteins are characterized by huge molecules of extreme complexity, and any modification of the unique structure of a native protein, giving rise to definite changes in chemical, physical, or biological properties, is termed denaturation. Protein denaturation may be caused by many agents or conditions, and in effect, may result in a product of quite variable quality. Since little is known concerning the true nature or structure of proteins, denaturation and its over-all effect on the quality of a food product is also poorly understood at the present time. The lack of basic information concerning adverse effects of freezing and cold storage on fishery products is an excellent example of this.

In view of the obvious lack of basic information on which to base more practical work, considerably more research is currently being carried out on fundamental studies of fish proteins. These studies can be classified in general as (1) studies on the rate and extent of denaturation of actomyosin both in the muscle and in the isolated state and (2) fractionation of fish muscle proteins and determination of the physico-chemical properties of the fractions.

<u>CHANGES IN PROTEIN SOLUBILITY</u>: Attempting to develop more objective methods for the measurement of frozen-fish quality, British workers applied to fish a procedure used earlier in classical studies on the proteins of rabbit muscle. They found a decrease in the solubility of the muscle proteins in salt solutions after frozen storage of the fish. On further investigation, Canadian workers showed that it was the protein fraction called actomyosin which lost its solubility in salt solutions and, by this criterion, was denatured, the non-actomyosin fractions remaining unchanged except after very long storage. From these observations, an objective method whereby the quality of frozen fish could be estimated was devised, namely, extraction of the soluble protein, followed by an estimation of the actomyosin content of the solution.

This method has received but limited application by various workers in the field of fishery research. In combination with taste-panel testing, precise work has shown that the actomyosin solubility appears to parallel and anticipate texture and flavor changes, thus providing a measure of the quality of a particular sample of fish. The drawbacks to the method are that it lacks considerable precision and provides no information as to the nature of the change involved.

<u>CHANGES IN PROTEIN VISCOSITY</u>: In an attempt to gain a better understanding of the adverse effects of freezing and cold storage on the quality of fish protein, changes in properties of the actomyosin fraction of fish muscle that has been subjected to frozen storage are being studied by this laboratory. The physical property of viscosity of protein solutions is the current phase of investigation. Since chemical changes in the fish protein alter the shape or size of the huge molecules, one clue to the extent of these changes is the absolute viscosity of a solution of the proteins. In order for a comparative study on the rate and extent of freeze denaturation of actomyosin to have any meaning, it is first necessary to establish the magnitude or nature of the sought-after property in the native actomyosin fraction from unfrozen fish. The work to date on this project has been concerned primarily with this aspect.

Accordingly, a method has been developed whereby the protein actomyosin is isolated from fish muscle and subjected to viscosity measurement, yielding a value which is a function of the asymmetry of the protein molecule. The following points have been established:

- (1) The precision of the method
- (2) The effect of time of storage at  $0^{\circ}$  C. on the actomyosin in the unfrozen muscle
- (3) The effect of time of storage at 0<sup>°</sup> C. on isolated actomyosin (from unfrozen muscle)
- (4) A function of the viscosity of native actomyosin which can be used as a standard to compare other states of the protein

Using the protein viscosity measurements and objective methods of texture comparison, a study on the rate and extent of freeze denaturation of actomyosin in fish muscle and its relation to the development of toughness is in progress. These studies are directed towards the improvement of objective methods of quality determination as well as improved handling and storage methods for frozen fishery products.

> --Harry L. Seagran, Biochemist, Fishery Products Laboratory, Fisheries Experimental Commission of Alaska, Ketchikan, Alaska

## A COMPARATIVE STUDY OF FISH MEALS MADE FROM HADDOCK OFFAL

The advent of freezing fish in-the-round at sea aboard the experimental freezing vessel <u>Delaware</u> provided an additional source of fish offal, in the form of viscera, to the regular fillet waste. This additional offal could well be a source of valuable byproducts. The regular fillet wastes (commonly called the frames) are usually reduced into fish meal. This, then, suggested one outlet for the utilization of the complete offal. The purpose of this project at the Boston Fishery Technological Laboratory was to determine the feasibility of preparing meals from fillet frames and viscera from haddock and scrod haddock frozen in-the-round at sea and to evaluate the physical, chemical, and biological properties of the resulting meals.

## December 1954

EXPERIMENTAL: Large quantities of haddock and scrod haddock were brine frozen in-the-round at sea aboard the Service's research trawler <u>Delaware</u>. Ashore, these fish were water-thawed, filleted in-the-round, and the offal, composed of the combined frames and viscera(excluding the skins from the fillets) was collected.

A minor portion of the offal was ground and frozen for the preparation of fish meals on a very small scale in the laboratory. Samples of the ground offal, in quantities of about two pounds each, were dried in an oven with circulating air at  $100^{\circ}$ C. (212° F.). A second small portion of the ground offal was dried in the laboratory by a solvent extraction process using ethylene dichloride.

The major portion of the offal was further divided into two portions and prepared into fish meal in two commercial plants employing different reduction processes. Delivery of the raw offal was made to the plants promptly after the fish were filleted and the offal collected. In the first reduction plant, 15,000 pounds of offal were cooked in a con-



Determining oil content of fishery byproducts.

tinuous cooker at 40 p.s.i. steam. The cooked offal was then pressed, in order to remove the stick liquors and fish oil, and then dried in a flame dryer in which the inlet air ranged from  $1300^{\circ}$  F. to  $1400^{\circ}$  F. In the second reduction plant, 10,000 pounds of offal were cooked in a steam-jacketed batch-type cooker for six hours at 100 p.s.i. steam. The cooked offal was then dried in a continuous steam-jacketed vacuum dryer for 45 minutes at 50 p.s.i. steam.

Laboratory-scale samples of fish meals were prepared from the frames of eviscerated haddock and scrod haddock. These fish had been iced at sea in the usual commercial manner. The frames were ground and dried by each of two methods: (1) in an oven at  $100^{\circ}$  C. (212° F.), and (2) by the solvent extraction method using ethylene dichloride.

All samples of meal produced were analyzed for proximate composition (moisture, protein, fat, and ash content).

<u>DISCUSSION</u> OF <u>RESULTS</u>: The data obtained are shown in table 1. The yield of fish oil is also included for those instances in which oil was recovered during the processing of the offal.

Meals made by the solvent-extraction process were of a light off-white color, had very little or no fish odor, and were quite dusty. Those meals prepared by commercial methods and by oven-drying were of a medium-brown color, had a slight fish odor, and were not appreciably dusty. The meal prepared by the commercialbatch process appeared to be "wet" with oil.

No difficulties were encountered in the commercial production of meal from the combined frames and viscera using the continuous process or the batch process of fish-meal manufacture.

The inclusion of the viscera in the offal did not materially affect the yield of fish meal over that obtained from the frames alone. The weight of the viscera represented approximately 27.5 percent of the weight of the combined frames and viscera. The addition of the visceral portions, now being thrown away, to the offal used would increase the raw material for fish-meal manufacture by about 38 percent and would

Table 1 - Yields Obtained and the Proximate Composition of Meals from Haddock Offal							
Description of the Samples of Meal		Yield of	Yield of	Composition of the Meal			
Raw Material	Processing Method	Meal	Oil	Moisture	Protein	Ash	Fat
Frames from eviscerated haddock iced at sea	Oven-dried at 100 <sup>°</sup> C.	$\frac{\text{Percent}}{20.6}$	Percent -	$\frac{\text{Percent}}{2.1}$	$\frac{\text{Percent}}{71.2}$	$\frac{\text{Percent}}{23.4}$	$\frac{\text{Percent}}{2.9}$
	Solvent-extracted $\frac{1}{2}$	19.8	0.75	2.1	73.9	23.6	0.24
Frames and viscera from round haddock frozen at sea	Oven-dried at 100°C.	21.1	-	2.0	53.1	23.9	18.6
	Solvent-extracted 1/	19.8	4.6	4.1	67.6	27.5	1.5
	Commercially continuous- cooked and flame-dried	18.2	2.0	7.9	59.3	26.0	4.9
	Commercially batch- cooked and vacuum-dried	19.5	-	7.3	53.5	23.1	18.9
1/ The solvent used was	s ethylene dichloride.						

be reflected in a proportionate increase in the amount of fish meal produced. However, the fish meal produced from the combined frames and viscera where the oil is not removed during the manufacture of the meal, as in the batch process, tends to be very oily and consequently low in protein.

Samples of the meals have been sent to the Service's Technological Laboratory at College Park, Md., for determination of their feeding value and, particularly, to determine the effect nutritionally of the viscera in the meals.

> --Joseph H. Carver, Chemist, Fishery Technological Laboratory, Branch of Commercial Fisheries, U. S. Fish and Wildlife Service, East Boston, Mass.



## CHESAPEAKE BAY--THE GREAT FISHING HOLE

The Chesapeake Bay is not infrequently termed the "Great Fishing Hole." This sobriquet is expressive in view of the following facts:

> Length - about 190 miles. Average width - 14 miles Greatest width - 35 miles. Total area - 4,316 square miles. Shore line - 4,500 miles Depth - one half of area is 20 feet or less with only onetwelfth 60 feet or more. Deepest point - 174 feet, just off southern tip of Kent Island.

Water volume - about 18,520,000,000,000 gallons. Drainage basin - 64,900 square miles.

--Maryland Tidewater News, December 1953.