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A Research Note EFFECT OF IRRADIATION ON VOLATILE CONSTITUENTS OF STORED HADDOCK FLESH

INTRODUCTION

IN RECENT YEARS the extension of shelf life of sea foods has received a great deal of consideration both in the United States and in many other countries of the world. In order to meet the world's growing need for fresh protein, even greater stability is required than refrigeration alone can provide. Since many commercial food fishes are taken from relatively cold waters, spoilage due to autolytic processes and microbial contamination of these food fishes continues even at cool temperatures. Thus the effectiveness of refrigeration for shelf life extension is reduced. It is most noticeable in the flavor of fresh fish, its most perishable characteristic.

Flavor deterioration in fish during storage is believed due primarily to microbial growth. Mendelsohn et al. (1966) have shown that the volatile compounds of stored haddock fillets increased with storage time and decreasing organoleptic quality. It would therefore be expected that objectionable flavor changes in fish could be diminished by γ -irradiation treatments that would materially reduce the microbial population in fish, especially since the active spoilage organisms are very susceptible to γ -rays. However, undesirable flavor changes in fish may be brought about by sterilizing doses of irradiation (Mendelsohn and Brooke, 1968).

Several other researchers have studied the effects of the irradiation process on sea foods. The effects of radiation on clam meats were studied by Gadbois et al. (1967) for development of carbonyl compounds and by Mendelsohn and Brooke (1968) for volatile compounds in the headspace vapors. Trimethylamine and amino nitrogen content measurements were made by Chung (1963). Novak and Luizzo (1963) studied the volatile fatty acids, carbonyl compounds and amino compounds in irradiated shrimp. Chemical changes attributed to low doses of radiation (radio-pasteurization) were found in all of these studies. Mendelsohn et al. (1969) have also shown, using gas chromatography, that both the number

and the concentrations of volatile compounds isolated and identified from haddock increased with increasing radiation dose. Nevertheless, Connors and Steinberg (1966) have shown organoleptic acceptability of haddock fillets irradiated at 150 and 250 Krad and stored from 0-30 days at $\approx 1^\circ\text{C}$. They also found that irradiation flavors and odors were not detected in any of the taste tests.

The purpose of this investigation was to study the effects of irradiation and storage on haddock fillets by analyzing the volatile constituents.

EXPERIMENTAL

FRESH HADDOCK FILLETS, obtained from a local dealer, were placed in mylar bags, sealed and irradiated at doses of 0, 0.2, 2.8 and 5.6 Mrad while keeping the fillets at $0-5^\circ\text{C}$. Samples from all treatments were taken immediately after processing. After storage at 5.5°C for 14 days, samples were taken of the fish treated at 0 and 0.2 Mrad. Samples of the fish treated at 0.2, 2.8 and 5.6 Mrad were taken after 30 days storage at 5.5°C .

Duplicate 1200-g samples of minced haddock flesh were prepared. The total condensate was collected from one of the 600g series (neutral) of the samples by low temperature-high vacuum distillation (Merritt et al., 1959) without further treatment. The remaining 600-g portions of each sample, forming a second series (alkaline), was first treated by adding 60 ml of 6N sodium hydroxide to the bottle, followed by adding 60 ml of distilled water and again mixing by shaking the bottle before collection of the total condensate in the same manner as for the first (neutral) 600g series of sample portions.

A "center fraction" (Merritt et al., 1959), or that fraction of the total condensate containing compounds exerting vapor pressure between the temperatures of -140°C and -80°C (most of CO_2 and H_2O removed), was separated from each of the total condensates obtained by low temperature-high vacuum distillation. All of these center fractions were analyzed by a combined programmed temperature gas chromatography and mass spectrometry instrument system (Merritt et al., 1966).

The components in the center fractions from the neutral sample portions were separated on a 50 ft \times 0.02 in. i.d. stainless steel support coated open tubular column with 1,2,3, tris

(cyanoethoxy) propane as the stationary phase and a helium carrier gas flow rate of 5 ml per minute. Separation of the components in the center fractions from the alkaline treated sample portions was achieved with a 10 ft \times 1/8 in. o.d. stainless steel column packed with 60-80 mesh chromasorb 103 coated with 10% carbowax 20M plus 3% KOH and a helium carrier gas flow rate of 20 ml per minute. The effluent of the gas chromatograph was eluted directly into the source of a Bendix Model 14 time-of-flight mass spectrometer. This mass spectrometer was equipped with several output devices including: a strip chart recorder to record the gas chromatogram of the sample by monitoring the total ion current of the mass spectrometer; a digital integrator for measuring the printing out both the area and retention time of each gas chromatographic peak; an oscilloscope for displaying the mass spectra; and a recording oscillograph for recording the mass spectra of each gas chromatographic peak as it elutes from the column. This output system made available both qualitative and quantitative data (Merritt, 1970).

RESULTS & DISCUSSION

THE COMPOUNDS found in both fresh and stored, irradiated and nonirradiated (neutral) haddock sample portions are listed in Table 1. These results show a few major differences between irradiated and nonirradiated samples. In general, more compounds were isolated from the irradiated samples than were isolated from the nonirradiated samples. This is expected, since irradiation causes many microchemical reactions in the fish flesh producing a wide variety of volatile compounds (Mendelsohn et al., 1969). Also, the irradiated samples contain more hydrocarbons. Few compounds were found in the sodium hydroxide treated samples. These compounds were methylamine, trimethylamine, dimethyl sulfide, methanol and ethanol; and they were found in all basic sample portions. The compound identities were the same for all irradiated samples as well as for all nonirradiated samples but varied greatly in amounts depending on irradiation dose and time in storage.

The overall results, reflecting the effects of radiation and storage on haddock fillets, combining the results of both the

neutral and basic sample portion series, are summarized in Figure 1. This figure shows only those classes of compounds that were found in large enough amounts in each sample to depict graphically. Amines, predominantly trimethylamine, were found in all basic sample portions regardless of storage time or radiation dose, even though the unstored haddock was judged to be fresh fish. This finding was true only for the basic sample portions and not for the neutral ones, indicating a release of trimethylamine by the addition of sodium hydroxide to the haddock flesh. Trimethylamine was found in the neutral sample portions only for the nonirradiated samples stored for 14 days. Nevertheless, before storage, higher concentrations of compounds were found, mostly hydrocarbons and sulfur compounds, in the irradiated haddock, the amounts being proportional to the irradiation dose. However, after storage, the nonirradiated samples contained the larger amounts of compounds, which are mainly sulfur and amine compounds with smaller amounts of carbonyl compounds and alcohols. It is also noticed that on

Table 1—Compounds identified from neutral sample portions of irradiated and nonirradiated haddock fillets

Irradiated		Non-Irradiated
butane	ethanal	ethanal
butene-1	2-me-propanal	2-me-propanal
pentane	butanal	butanal
pentene-1	2-me-butanal	2-me-butanal
methylpentane	acetone	acetone
hexane	butanone-2	methanol
hexene-1	methanol	ethanol
heptane	ethanol	ethyl mercaptan
heptene-1	ethyl mercaptan	dimethyl sulfide
octane	dimethyl sulfide	dimethyl disulfide
benzene	dimethyl disulfide	methylamine
toluene		trimethylamine
		benzene
		toluene

storage, the hydrocarbons and other compounds formed by irradiation diminish in quantity, especially the more volatile ones. This is believed due to the permeability of these gases through the mylar

package. It can also be seen that the samples treated with the lower irradiation doses formed sulfur and amine compounds on storage, but not to the extent of the nonirradiated samples.

Haddock irradiated at 0.2 Mrad shows an increase in volatile material with storage time although the increase is smaller than the nonirradiated haddock samples. This clearly indicates that although the microbial population is vastly decreased by this low irradiation dose, the haddock flesh is by no means sterile. The sterilized sample (5.6 Mrad) shows a sharp decrease in volatile compounds on storage. Samples irradiated at 2.8 Mrad also show a decrease in volatile compounds during storage although not as sharply as when irradiated at 5.6 Mrad. This indicates that although 2.8 Mrad is not a high enough dose for sterilization, it has decreased the microbial activity to such an extent that the overall losses of volatile compounds in this dynamic system exceed microbial production of volatile constituents during storage.

Sensory evaluations were not performed in this study. However, on comparing the processing and storage conditions in this study with those in studies where sensory evaluations were performed, some interesting correlations may be drawn. Since Connors and Steinberg (1966) stated that the taste panel used in that study did not indicate the presence of irradiation flavors or odors in any of the samples, which included doses as high as 0.35 Mrad; the unstored samples irradiated at 0.2 Mrad in this study would not be expected to possess an irradiated flavor. Connors and Steinberg (1966) have also shown that haddock fillets irradiated at 0.25 Mrad were still organoleptically acceptable after 30 days in storage at 1°C, although acceptability decreased after 20 days in storage. Since the irradiation dose and storage condi-

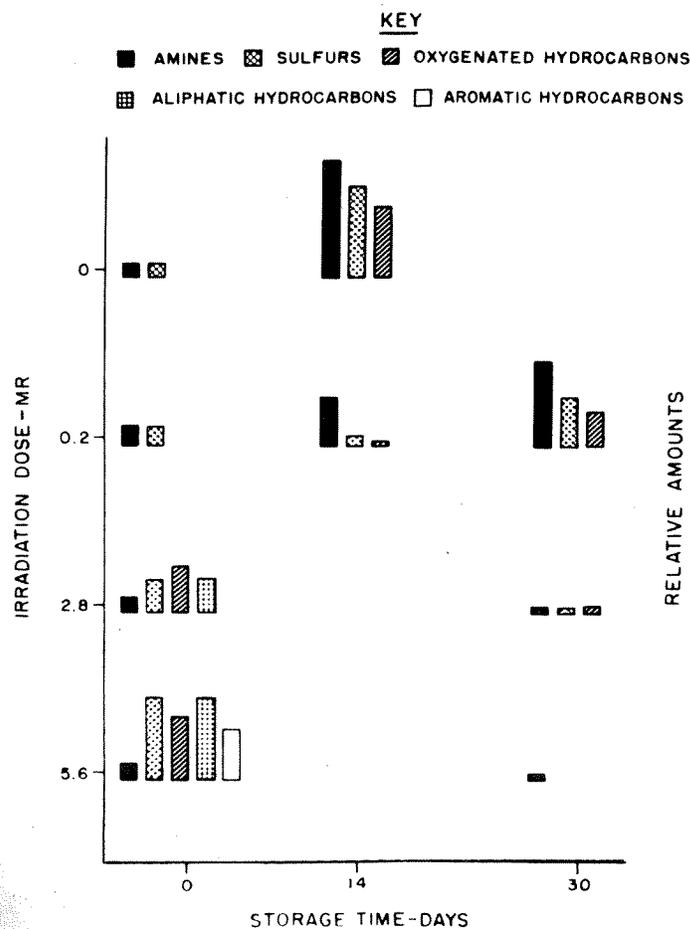


Fig. 1—Relative amounts of classes of volatile compounds found in stored haddock fillets.

tions for the study by Connors and Steinberg (1966) are similar to those in this study for the 0.2 Mrad irradiated samples, it would be expected that the extent of the increase in concentrations of volatile compounds found after 14 days of storage would indicate no decrease in organoleptic acceptability, whereas the extent of the increase in concentrations of volatiles in the samples stored for 30 days would indicate a decrease in organoleptic acceptability.

Ronsivalli et al. (1968) point out the pronounced organoleptic changes brought about in fish by sterilization doses of ionizing radiations. Such changes would be expected in the haddock fillets sterilized by irradiation with a dose of 5.6 Mrad in this study. This is consistent with the relatively high concentration of volatiles, especially sulfur and carbonyl compounds found for the unstored haddock fillets irradiated at 5.6 Mrad in this study. Although the concentration of volatiles in the haddock fillets irradiated at 2.8 Mrad was considerably lower than in the samples irradiated at 5.6 Mrad before storage, they probably contained a high enough concentration of volatile compounds to alter the organoleptic quality of the fillets. However, after 30 days in storage under the conditions used in this study, the samples irradiated at 5.6 Mrad and 2.8 Mrad both contained lower concentrations of volatile compounds than did the samples irradiated at 0.2 Mrad. In view of these findings it would be expected that the samples analyzed in this study irradiated at 2.8 Mrad and perhaps even those irradiated at 5.6 Mrad at 5°C and stored at refrigerated temperature

could have good organoleptic quality. Mendelsohn et al. (1970) also found cod fillets to be organoleptically acceptable after irradiation at 4.5 Mrad at cryogenic temperatures. Although it must be kept in mind that production of volatile compounds is not the only change affecting organoleptic quality that would be initiated by ionizing radiation, it can serve, however, as a good indicator for the extent of change which has occurred.

CONCLUSIONS

CONSIDERING these results and related studies (see references) it may be concluded that:

1. The microbial deterioration of chill-sotred haddock can be reduced by irradiation which decreases the spoilage microorganisms and thereby the shelf life of haddock is increased.

2. If an odor is caused by volatiles formed in irradiated haddock, it probably decreases with storage time if the product is packed in a gas permeable container.

3. The types and overall patterns of compounds produced by irradiation and microbial deterioration of fish are quite similar but differ significantly with respect to hydrocarbons and amines.

4. The expected shelf life at a given storage temperature would depend on the irradiation dose.

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