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Comparison of TBA Number of Irradiated Fish With Sensory Quality

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ABSTRACT

A steam distillation method for the determination of the TBA number in control and irradiated hake and tuna is presented. Chemical values are compared with sensoric evaluation results for the 30-day cold storage period. Close correlation has been observed between the organoleptic scores and the oxidative rancidity in tuna loins and hake fillets, whether control or irradiated.

INTRODUCTION

During the cold storage of fish, oxidizing processes change the physical and chemical parameters that govern its organoleptic characteristics

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(Quaranta *et al.*, 1984*a*). The end products of these oxidative reactions are usually tested using the direct thiobarbituric (TBA) extraction method (Vynke, 1970, 1975; Hussain *et al.*, 1978; Curzio & Quaranta, 1982; Quaranta *et al.*, 1984*a*). In the TBA test, which is widely used in the evaluation of the extent of oxidative rancidity processes in fat-containing foodstuffs (i.e. fatty fish products), rancidity is expressed in terms of the TBA number (milligrams of malonaldehyde per kilogram of sample).

Malonaldehyde is a product of autooxidation processes in polyunsaturated fatty acids and is a highly reactive dicarbonyl (Kakuda *et al.*, 1981) which condenses with two molecules of TBA (2-thiobarbituric acid) yielding a coloured complex responsible for the absorption peak at 535 nm (Sinnhuber *et al.*, 1958; Schmidt, 1959).

The most common procedure for the TBA test is to homogenize the food sample with 9·0 % trichloroacetic acid solution which also contains 0·12 % of both propylgallate (PG) and ethylenediaminetetraacetic acid (EDTA). After filtering an aliquot, the extract is allowed to react with the TBA reagent and colour is developed by heating for 40 min in a boiling water bath. Absorbance of the resulting coloured complex is directly read at 535 nm in a spectrophotometer using 1 cm path length cells (Vyncke, 1970; Curzio & Quaranta, 1982; Quaranta *et al.*, 1984*a*).

Curzio & Quaranta (1982) reported the use of this extraction method in the evaluation of oxidative rancidity in hake fillets; Vyncke (1970, 1975) evaluated the possibilities of this method in trichloroacetic acid extracts of redfish, cod, mackerel, plaice, spurdog and herring and Quaranta *et al.* (1984*a*) found it useful for malonaldehyde evaluation in tuna fish loins. Witte *et al.* (1980) also reported favourable results on pork and beef using an extraction mixture of trichloroacetic acid and phosphoric acid.

The disadvantages of the direct TBA extraction method are numerous: the extract of the fish muscle is not always clear, it is a time-consuming procedure, the muscle is extracted with a concentrated TBA reagent that may lead to side reactions during the colour-forming step and, finally, the reagent interacts with the whole fish flesh, increasing the possibility of reaction with interfering compounds.

Steam distillation methods for the extraction of malonaldehyde from acidified food solutions were suggested by some investigators (Sidwell *et al.*, 1955; Tarladgis *et al.*, 1960; Witte *et al.*, 1980).

Because of drawbacks with the direct TBA extraction method, adaption of a steam distillation procedure with colorimetric final

determination was carried out, in order to determine the oxidative rancidity in hake and tuna fish flesh.

MATERIAL AND METHODS

Fish samples

Tuna and hake came from the fishing grounds of the Argentinean platform (South Atlantic Ocean) and were caught by commercial vessels. Fishes were kept on ice after being caught and conditioned for market at commercial facilities on land.

Hake were filleted three days after being caught and tuna loins were taken from fish deboned after four days in ice. Both hake fillets and tuna loins, were quick-frozen to $-30\,^{\circ}C$ in a plate freezer and then sealed in 100 μm thick polyethylene bags (250 g each); hake and tuna samples were stored in a commercial freezer at $-18\,^{\circ}C$ until irradiation the day after. Half of each batch was irradiated, the remaining samples being used as a control. Following irradiation, both irradiated and control hake and tuna loins were stored at 4–6 °C in a commercial refrigerator and removed periodically for the evaluation of malonaldehyde content.

Irradiation process

A Phillips X-ray machine was used to irradiate the samples to a dose of 220 krad (2·20 kGy). This dose level was suggested by an expert panel from the Joint FAO–IAEA–WHO and yielded good results in previous experiments (Quaranta *et al.*, 1984*a*,*b*; Quaranta *et al.*, 1984*c*).

Apparatus

Distillation
Steam distillation apparatus (distillation rate of 10 ml/min).

Spectrophotometry
Beckman DU spectrophotometer with 1 cm path length stoppered quartz cells.

Reagents

Tetraethoxypropane
A stock solution of 20 mg of tetraethoxypropane (Sigma) in 100 ml of distilled water.

TBA reagent
0·02M 2-thiobarbituric acid (Merck) solution.

Procedure

Determination of the malonaldehyde content was carried out as follows. Triplicates of approximately 30 g of tuna fish loins and hake fillets, representative of the whole sample, were homogenized with 90 ml of 10% trichloroacetic acid solution using a household blender, and the homogenate was transferred to the distillation apparatus where it was steam distilled for 15 min. Calibration of the spectrophotometer was carried out, evaluating the TBA number of 100-ml water samples containing 0, 0·2, 0·4, 0·6, 0·8 and 1·0 ml of the tetraethoxypropane stock solution.

The assay proceeds by allowing 2·5 ml 0·02M 2-thiobarbituric acid to react with 2·5 ml of the distillate and 2·5 ml of each standard solution in test tubes with Teflon sealing screw caps; colour was developed during 40 min in a boiling water bath and then the tubes were cooled in tap water; absorbance was read at 535 nm by means of a spectrophotometer.

The results were expressed as micrograms of malonaldehyde per kilogram of fish sample. For calculation purposes recovery was determined to be 92% and this was taken into account.

Sensoric evaluation

Organoleptic quality was recorded for both irradiated and control hake and tuna throughout the whole storage period. Sensoric evaluation of the samples was carried out by a five-judge taste panel: portions (*ca.* 50 g) of raw and boiled tuna and hake meat, from both irradiated and control batches, were given to the panellists, who scored sensoric characteristics such as texture, odour, colour, taste (boiled), presence of exudate and overall appearance using the 9-point hedonic scale. The judges were also asked to rank the samples using general acceptability as a parameter, according to the methods described by Quaranta & Pérez (1982*a*,*b*).

RESULTS

Table 1 shows the average contents of water, lipids, proteins and ash arising from the chemical analysis of hake fillets and tuna loins. Tables 2 and 3 present the evolution of malonaldehyde content in control and irradiated hake fillets and tuna loins, respectively.

For hake fillets, the initial values for control and irradiated fish were 215 ± 19 and 412 ± 32 μg malonaldehyde per kilogram of sample, while the maxima were 1768 ± 106 and 1596 ± 87 μg malonaldehyde per kilogram of fish, respectively observed 12 days (control) and 24 days

TABLE 1
Composition of Hake and Tuna Fish Flesh[a]

	Hake fillets (%)	*Tuna loins* (%)
Water	80·2	77·9
Lipids	1·3	2·7
Proteins	17·2	17·9
Ash	1·2	1·4

[a] Sources: Curzio & Quaranta (1982); R. A. Rothe, private communication (1983).

TABLE 2
Evolution of the TBA Values during Cold Storage of Unirradiated and Irradiated Hake Fillets. Experimental Points are the Average of Three Determinations

Days	*Micrograms of malonaldehyde per kilogram of fish*	
	Irradiated	*Unirradiated*
0	412	215
4	503	390
8	579	721
10	1024	1374
12	1130	1768
16	1227	1483
21	1407	1097
24	1596	874
26	1210	681
30	790	617

TABLE 3
Development of the Malonaldehyde Content during Cold Storage of Unirradiated and Irradiated Tuna Fish Loins. Experimental Points are the Average of Three Determinations

Days	*Micrograms of malonaldehyde per kilogram of fish*	
	Irradiated	*Unirradiated*
0	542	374
4	720	871
8	805	1960
10	1031	2394
12	1160	1702
16	1257	1240
21	1477	927
24	1824	674
26	2030	609
30	1589	571

(irradiated) after treatment; the difference between the initial TBA values for control and irradiated samples was significant.

For tuna loins the initial value for control samples was $374 \pm 27\,\mu g$ malonaldehyde per kilogram whilst, for irradiated tuna, the TBA value was $542 \pm 36\,\mu g$ malonaldehyde per kilogram of fish. The maximum for control tuna was $2394 \pm 160\,\mu g$ malonaldehyde per kilogram, observed after 10 days in cold storage, whilst for irradiated samples, the maximum

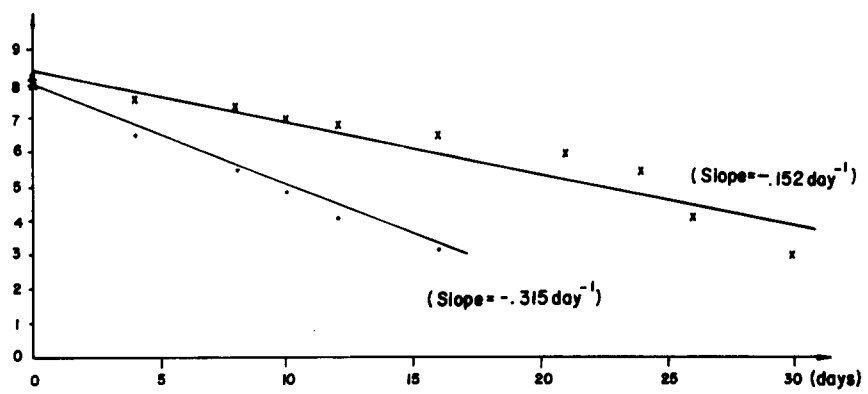

Fig. 1. Organoleptic scores of irradiated and control hake fillets during storage at 4–6 °C; (●) control, (×) irradiated (2·20 kGy).

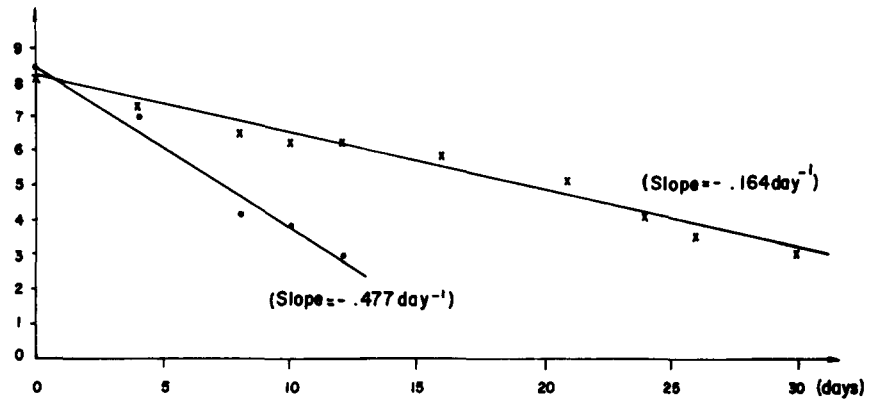

Fig. 2. Sensoric scoring for irradiated and control tuna loins during storage at 4–6 °C; (●) control, (×) irradiated (2·20 kGy).

value was 2030 ± 139 μg malonaldehyde per kilogram of fish, 26 days after irradiation. The difference between the initial TBA values for control and irradiated tuna was also significant.

Figures 1 and 2 show the regression lines for sensoric records throughout the storage period for both treatments in hake fillets and tuna loins, respectively.

In sensory evaluation, the taste panel judged as unacceptable (4 on the 9-point hedonic scale) all the control hake samples after 8 days of cold storage, while the irradiated hake fillets showed acceptable scores (6·0 points) until the twenty-first day. In judging tuna samples, the control was reported to be unacceptable after the eighth day in the cold while irradiated tuna remained in good organoleptic condition 16 days after treatment.

DISCUSSION

From Table 1, where the TBA values (or malonaldehyde content) of control and irradiated hake fillets are shown as a function of the time that the fish had been stored in the cold, it can be seen that measured values tend to increase with time, reaching a maximum on the twelfth (control) and the twenty-fourth (irradiated) days of cold storage; this is followed by a decline until the end of the storage period. From Table 2, where the malonaldehyde content in both control and irradiated tuna loins is tabulated against the days that the fish had been kept in the cold, there is

also a trend of increasing TBA values with storage time, followed by a decline in the 10-day old (control) and 26-day old (irradiated) samples. The delay in reaching the malonaldehyde peak in the irradiated hake and tuna samples was consistently observed in different experiments. Similar behaviour was observed by Hussain *et al.* (1978) in their studies with various fish species and by Curzio & Quaranta (1982) when studying the oxidative rancidity of hake fillets using the direct TBA extraction method. Similar results were also reported by Quaranta *et al.* (1984*a*) with tuna. The decline after the maximum can be attributed either to the interaction of thiobarbituric acid-reactive products with other volatile tissue constituents, or to malonaldehyde utilization by surviving micro-organisms.

Close correlation has been observed between the organoleptic scores and the malonaldehyde content of tuna loins and hake fillets, either control or irradiated; unacceptable sensoric scores were obtained just before the MA content reached the maximum.

In both control and irradiated hake, the malonaldehyde content throughout the whole storage period was lower than the amount for tuna loins. This can be explained by the fact that tuna has a higher fat content than hake, as is shown in Table 1.

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