Extending the Shelf Life of Brown Shrimps (Crangon vulgaris Fabr.) by Gamma Irradiation

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(Received October 5, 1971, lwt 143)

Irradiation experiments with doses ranging from 0,05 to 0,5 Mrad were carried out to study the influence of radiation pasteurization on the quality and shelf life of brown shrimps. The shrimps were cooked at sea in the usual manner, packed in paper bags and wrapped in stretch film before irradiation.
After irradiation they were kept at 0°C. At regular intervals the following objective quality indices were determined: total volatile basic nitrogen, trimethylamine, dimethylamine, ammonia, volatile acids, volatile reducing substances, redox potential, α-amino nitrogen, hypoxanthine, total bacterial count, psychrophilic and anaerobic bacteria.
These tests and the organoleptic judgment showed the shelf life of brown shrimps to be extended by at least 12 days by gamma irradiation. The optimal dose appeared to be 0.1 Mrad. Radiation pasteurization gave slight taste and odour changes in some experiments, due to fortuitous changes in treatment before irradiation, but this did not influence the overall acceptability of the product.
With doses of 0.3 Mrad and higher, unacceptable off-flavours were noted.
Especially TVN and ammonia appeared to be fairly reliable indices of spoilage of irradiated shrimps.

Introduction

The brown shrimp (*Crangon vulgaris* Fabr.) is an important and highly priced crustacean in Western Europe. During the past five years, landings averaged 19 000 tons per year in W.-Germany, the Netherlands, the United Kingdom, France and Belgium for a sum of 12 million dollars.

Due to a high content of extractable nitrogen compounds, an active proteolytic enzyme system (which is not always fully destroyed in the boiling process) and a relatively large body surface, the brown shrimp constitutes a favourable substrate for micro-organisms and therefore becomes a highly perishable product with a shelf-life of only a few days. For longer storage periods, the use of an antiseptic (usually benzoic acid or its salts) is necessary although it alters the delicate flavour of the brown shrimp and its effectiveness is limited.

Changes also occur, albeit to a lesser extent, while freezing or freeze-drying, the latter method being furthermore rather expensive.

Another preservation possibility is the use of ionizing irradiation. Many studies in the past decade have shown that seafood is one of the most promising food groups for this preservation method. Hence, experiments were started in collaboration with the Belgian Centre for the Study of Nuclear Energy (SCK-CEN, Mol, Department of Radioisotopes) and the Laboratory of Food Preservation of the University of Louvain in order to evaluate the possibilities of radiopasteurization for prolonging the shelf life of brown shrimp. This paper reports the results of two series of experiments on unpeeled cooked shrimps with doses ranging from 0.05 to 0.5 Mrad. Another aim of this study was to investigate the usefulness of different commonly employed objective quality methods for irradiated shrimps.

Radiation was carried out about 40 and 16 hours after the catch in the first and second series of tests respectively.

Materials and Methods

Shrimps

The shrimps were caught by a commercial beam trawler off the Belgian coast and cooked for 6 to 10 min. (average: 7 min.) in brine. They were carefully cooled for about 8 min. and kept in polyethylene kits without further refrigeration until the arrival in the harbour, about 6 hours after the catch. They were of the so-called "salt type", the salt content of the meat being 3 to 3.5 %.

Methods

- Total volatile bases (TVN): by the method of LÜCKE and GEIDEL (1) as modified by ANTONACOPOULOS (2).
- Trimethylamine (TMA): according to DYER (3) but an 2 ml of distillate of the TVN-determination.
- Dimethylamine (DMA): according to DYER and MOUNSEY (4) but on 10 ml of the TVN-distillate.
- Ammonia: by accelerated microdiffusion (5).
- Total volatile acids (VAN): by the method of the AOAC (6) but using ANTONACOPOULOS' still (7); 500 ml were distilled over.
- Volatile reducing substances (VRS): according to FARBER and FERRO (8). The shrimp juice was obtained by pressing the samples in a small press with conical discs (9).
- α-amino nitrogen: by the copper method of POPE and STEVENS (10) on a trichloracetic acid extract.
- Hypoxanthine: according to JONES et al. (11).
- Redox potential: determined on press juice, under an atmosphere of nitrogen using a combined platinum-calomel electrode. Potential was read after exactly 5 min. and expressed as mV against the calomel reference electrode.
- Microbiological determinations: Total aerobic, anaerobic

and psychrophilic microflora counts were made by inoculation in Petri dishes containing Plate Count Agar (Difco). For total counts incubations lasted for 72 hrs at 20–22°C. The GasPak anaerobic system (B.B.L., Cockeysville, Maryland, USA) was used for anaerobic counts. Incubations lasted for 72 hrs at 30°C. Psychrophilic bacteria were determined after a 12 days' incubation period at 4–6°C.

– Organoleptic judgment: was performed by a panel of four members on colour, texture, odour and taste using the following scoring system: 5: excellent; 4: good; 3: moderate; 2: borderline; 1: bad, 0: very bad.

Procedure
The shrimps were packed in paper bags of 1 kg each which were then wrapped in polyvinylchloride stretch film to prevent desiccation. The samples were kept at 0°C during transport and storage. In a first series of three tests, carried out during spring, the shrimps were irradiated about 40 hrs after catch; they were then stored again at 0°C and samples were taken at regular intervals for analysis. This series was considered as a general guidance experiment and the number of tests run on the different samples was limited (TVN, TMA, VAN, ammonia and VRS). In a second series of three experiments, carried out in autumn, the same procedure was used, but the time delay before irradiation could be reduced to ca. 16 hrs. Additional analyses (DMA, hypoxanthine, redox potential, α-amino nitrogen and bacterial counts) were included.

Irradiation
Radiopasteurization was carried out in a research irradiator consisting of a watertight container lowered between a 60 Co source stored in the hydraulic channel of the BR2 reactor at the Mol Nuclear Centre. Five kg of shrimps were irradiated and the measured overdose ratio was 1.3 (12). The importance of accurately determining this ratio and of keeping it at a minimum level was stressed by LEONE (13) and SCHIETECATTE (14). In the first series, doses of 0.1, 0.2, 0.3 and 0.5 Mrad were used. In the second series, 0.05, 0.1 and 0.2 Mrad were chosen. Owing to the short irradiation time (15 min. per 0.1 Mrad), the temperature of the shrimps increased by only a few degrees.

Results and Discussion

The different spoilage patterns of the individual experiments being fairly similar, average values were calculated for the sake of concision.

Irradiation experiments after 40 hours' delay
Organoleptic judgment **(Fig. 1)** showed that irradiation had a marked effect on the shelf-life of the shrimps. With doses of 0.3 and 0.5 Mrad however, an acidic off-flavour ("irradiation flavour") was noticed, which was judged to be unacceptable; results of these too high doses were not reported on **Fig. 1.**
Sensory scores of the 0.1 and 0.2 Mrad experiments respectively were very similar. In our experiments, an organoleptic score of 3 ("moderate") was set as quality limit. This value was reached after 24 (± 2) days in the irradiated samples and after 9 (± 1) days in the others. The first samples were considered spoiled after approximately 32 days, the second ones after ca. 13 days. It was further noted that in one experiment a slight irradiation odour and -taste appeared after 11 days of storage. This will be discussed further.

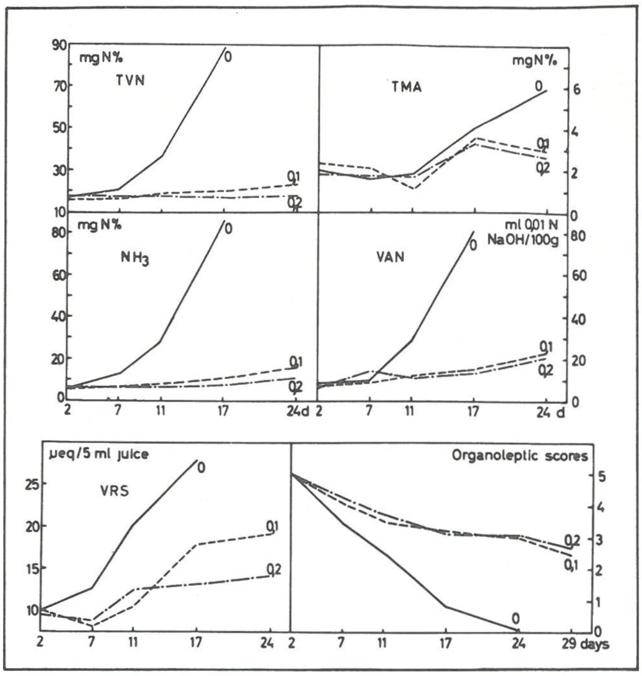

Fig. 1 Chemical and organoleptic analyses of irradiated shrimps. (0,1 and 0,2 Mrad; control [0])

Colour of the irradiated shrimps remained unchanged. This was confirmed by chemical analyses carried out at the Laboratory of Food Preservation (University of Louvain) where it has been shown that the carotenoid pigments of the brown shrimp are remarkably stable towards irradiation (15) giving similar results as with other crustacea and contrasting in this respect with the pigments of other fishery products such as salmon (16).
Finally, it was experienced that the shells of the unpeeled cooked shrimps became rough and rather dry after three to four days, both in the irradiated and the control samples, probably due to chemical modifications of the chitin. Nevertheless, peelability was excellent and the peeled shrimps were of good quality. This phenomenon can be inhibited chemically (e.g. by polyphosphate dips) but this was not the purpose of the present work.
The results of the TVN, VAN, VRS and ammonia determinations **(Fig. 1)** carried out until de 24th day, corresponding with a sensory score of 3, confirmed the organoleptic judgments. There was no marked difference between the 0.1 and 0.2 Mrad doses, except to some extent with the VRS test. Individual determinations (not quoted) however varied more with this test than with others.
Non-irradiated samples showed similar steep spoilage curves, contrasting with the curves of the radiopasteurized shirmps.
Neither the TMA values of the untreated samples nor those of the irradiated samples correlated with the organoleptic judgment and remained at an unexpectedly low level, especially in the definitely spoiled shrimps. This confirms previous observations that the TMA determination is a rather poor objective quality test for cooked shrimps (17).
For the reason mentioned above, data of the 0.3 and 0.5 Mrad experiments were not reported in the graphs, but they were very similar with the results of the 0.3 Mrad samples.

Irradiation experiments after 16 hours' delay
Organoleptic judgment confirmed the results of the first series of tests. Even with 0.05 Mrad, a marked improvement in shelf life was noted, although this was slightly less than

with the 0.1 and 0.2 Mrad doses. The organoleptic score of 3 was reached after 24 (± 2) days for the samples irradiated with doses of 0.1 and 0.2 Mrad and after 19 (± 2) days for the 0.05 Mrad shrimps. The non-irradiated lots reached that value after 10 (± 1) days. The 0.1 and 0.2 Mrad samples were considered spoiled after approximately 33 days, the 0.05 Mrad samples after about 29 days and the untreated shrimps after ca. 14 days.

As in the first series, a slight irradiation odour and -taste was noted in one experiment. The reason for this might be sought in some fortuitously modified processing method on board. LUDORFF et al. (18), DEGKWITZ et al. (19), MEYER-WAARDEN (20), MANN (21) and van SPREEKENS and de MAN (22) stressed the importance of the processing method and especially of the cooking procedure on the quality and shelf life of the shrimps. It is not always easy on deck at sea to obtain an equal degree of boiling. Evidence was gained that cooking time is at least one important factor for avoiding irradiation flavour. The opportunity was given to irradiate two batches of shrimps which had been cooked for only 3 or 4 min. against 6 to 10 min. in the "normal" procedure. Both lots of shrimps showed the characteristic irradiation taste and -smell after a few days' storage. Another possibility is the presence of other marine specimens in the catch which are accidentally cooked together with the shrimps. ROSKAM (23) reported the influence of a small fish (*Gobius minutus*), which covers the shrimps with slime and extruded waste matter from its intestines, on the quality of the crustacean.

The influence of irradiation on the spoilage of shrimps is clearly shown by the results of the different laboratory analyses (**Fig. 2**). Of the chemical methods, TVN, ammonia and DMA correlated best with organoleptic judgment, giving e.g. higher values after a 16 days' storage period for the 0.05 Mrad dose. DMA was found in only very small amounts. It should be emphasized that the formation of this base by irradiation cleavage of trimethylamineoxide in different fishery products but especially in gadoid fish was reported by AMANO and TOZAWA (24). This was obviously not the case with *Crangon vulgaris* indicating that the specific enzyme system involved in the reaction was absent. The necessity of this system was demonstrated by the cited Japanese authors.

Oxido-reduction measurements may give useful information on bacterial activity. From **Fig. 2** it appears that the redox potential quickly decreased in non-irradiated shrimps to reach a minimum level of ca. 10 mV after 15 days; it remained practically unchanged in the irradiated samples. When comparing these results with bacteriological data (**Fig. 3**) it appears that the redox potential was mainly determined by the activity of the specific spoilage flora (not further studied in this work) and not by the total microbial flora.

Free amino acids decreased markedly in the untreated shrimps, indicating that the activity of bacterial desaminases was stronger than that of the endo- and exopeptidases. This is in good agreement with the increase of ammonia (**Fig. 2**). Desamination was inhibited by radurization but there was no clear difference between the three applied doses.

As to be expected, radiopasteurization markedly decreased initial bacterial load. The reduction depended on irradiation dosis and ranged from about 10^2 to 10^4. Similar reductions were obtained by other authors on different cooked or blanched crustacea (25–30). Psychrophilic bacteria showed practically the same pattern as total bacterial counts, indicating that about the whole microbial flora was of a psychrophilic nature. The further increase of bacterial

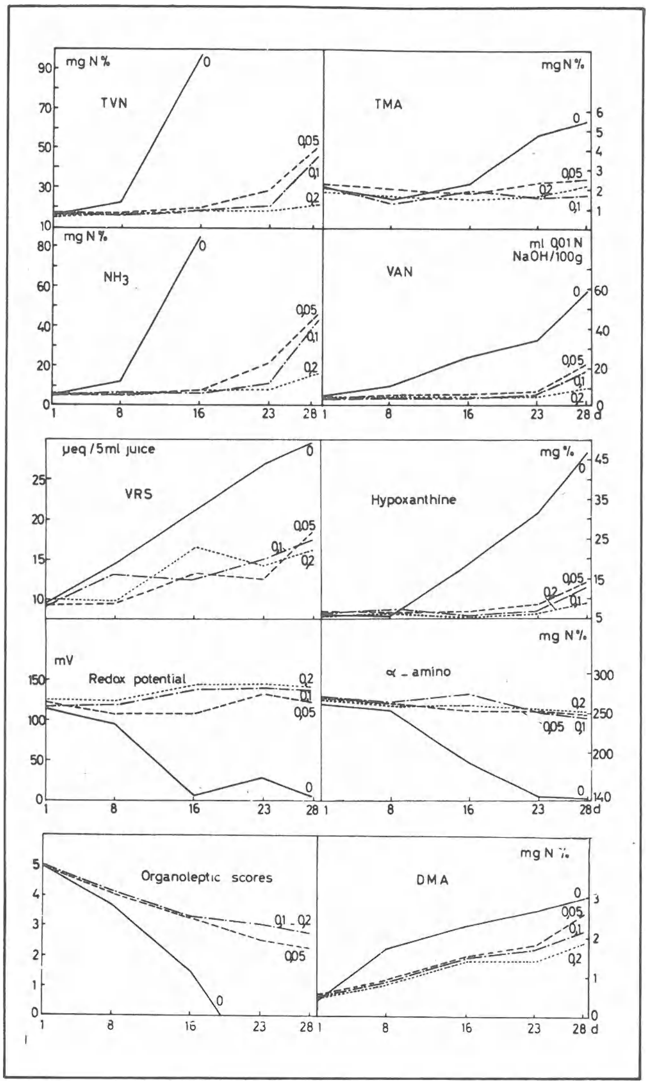

Fig. 2 Chemical and organoleptic analyses of irradiated shrimps. (0,05–0,1 and 0,2 Mrad; control [0])

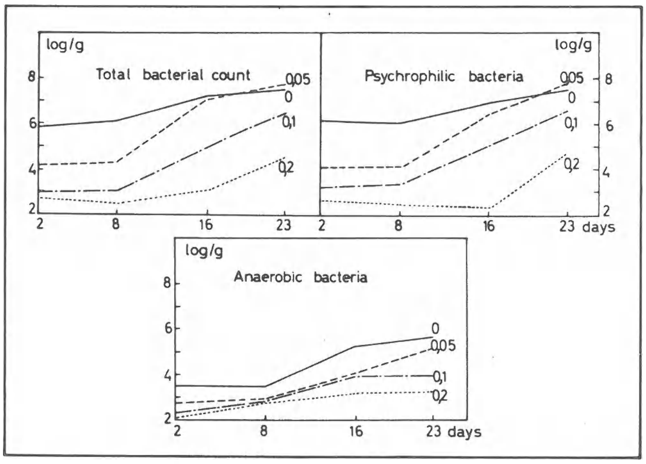

Fig. 3 Bacteriological analyses of irradiated shrimps. (0,05–0,1 and 0,2 Mrad; control [0])

counts during storage correlated neither with organoleptic judgment nor with most chemical analyses. The shrimps treated with 0.05 Mrad doses even achieved higher levels than non-irradiated shrimps at the end of the storage period. This phenomenon was also observed on different fishery products by other workers (27, 29, 31–34). SLA-

VIN et al. (31) suggested that it might be due to the post-irradiation flora being less metabolically active so that greater numbers are needed to produce an equivalent amount of spoilage. The same authors (27, 29, 31–34) also emphasized that gamma irradiation radically alters, both qualitatively and quantitatively, the microbial flora of fish and other seafoods. This was once again confirmed by these experiments on *Crangon vulgaris.*

Anaerobic counts showed a somewhat better agreement with organoleptic and chemical tests but were of few practical value.

When comparing the results of both series of experiments, only a slight difference in keeping quality in favour of the 2nd series was observed between the shrimps irradiated with 0.1 or 0.2 Mrad, as reflected by organoleptic and chemical analyses. The supplementary delay of 24 hrs before gamma irradiation did not seem to influence further shelf-life significantly. How long this time delay can still be prolonged should be investigated in further experiments.

When considering the value of the applied objective quality methods, TVN, ammonia, and to some lesser extent VAN and DMA appeared to be fairly reliable methods for assessing spoilage of irradiated shrimps. It should be emphasized that two widely used tests such as TMA and total bacterial counts were not reliable indices of quality. This was also reported recently for tropical shrimps (*Penaeus* sp.) by KUMTA et al. (29) who found on the other hand that TVN correlated fairly well with organoleptic observations. It can be added that the suitability of the objective quality methods seems to depend on the nature of the irradiated product and the processing variables before radurization. SPINELLI et al. (35) indeed reported that total bacterial counts, VAN, hypoxanthine and TMA correlated with sensory changes for several species of fish. HANNESSON and DAGBJARTSSON (30) on the other hand recently reported that TMA and VAN were unreliable methods for irradiated Norway lobsters (*Nephrops norvegicus*) and deep-sea shrimps (*Pandalus borealis*) but that total bacterial counts were in fairly good agreement with sensory evaluation.

Acknowledgment

The authors wish to thank Prof. **E. Maes, P. Tobback** and **F. Snauwaert** (University of Louvain) and **W. Schietecatte** (SCK-CEN, Mol) for useful advise and collaboration.

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