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A REVIEW OF THE CHEMICAL ASPECTS OF IRRADIATED SHRIMP

ETUDE DES ASPECTS CHIMIQUES DE CREVETTES IRRADIEES

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RÉSUMÉ

La bibliographie a servi à renseigner sur les aspects chimiques de crevettes irradiées. L'irradiation à faible dose peut limiter efficacement la détérioration et les organismes pathogéniques et augmenter la durée de conservation en magasin, à l'état réfrigéré, des crevettes. Une augmentation, par irradiation, du noircissement se produit chez certaines espèces au cours de la conservation mais on peut la minimiser par un blanchiment convenable. Il y a une certaine perte de la couleur rose caractéristique à une dose supérieure à 2,5 kGy et de mauvaises odeurs dues à l'irradiation à un dose supérieure à 1,5 kGy. On peut minimiser ces changements en irradiant les crevettes à l'état congelé. Il n'y a aucun changement important de la teneur en protéines, matières grasses, glucides et cendres du fait de l'irradiation à faible dose. L'irradiation à faible dose n'entraîne aucun changement décelable de la concentration de composés carbonylés volatils; l'irradiation à 8 kGy entraîne une augmentation transitoire de la totalité des composés volatils au cours de la conservation ultérieure dans la glace mais l'augmentation est plus forte chez les crevettes non irradiées. Les changements par irradiation de la composition des acides gras de crevettes sont faibles. Il y a certains changements faibles de la composition des acides aminés de crevettes irradiées; il y a des changements semblables par d'autres procédés tels que la mise en conserve et le séchage à l'air chaud. Certaines vitamines de crevettes telles que la thiamine sont influencées par l'irradiation. Mais la perte est moins grande que chez les crevettes traitées à la chaleur. Le rapport de rendement de protéines n'est pas influencé par l'irradiation des crevettes et on n'a constaté aucuns effets nuisibles par l'irradiation lors des études d'alimentation d'animaux.

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ABSTRACT

The literature was reviewed for information on the chemical aspects of irradiated shrimp. Low-dose irradiation can effectively control spoilage and pathogenic organisms and extend the refrigerated shelf life of shrimp. Radiation-induced increases in black discoloration occur in some species during storage, but can be minimized by proper blanching. Some loss of the characteristic pink color occurs at doses above 2.5 kGy, and irradiation off-odors occur above 1.5 kGy. These changes can be minimized by irradiating the shrimp when they are frozen. No significant change in protein, fat, carbohydrate, and ash content occurs as a result of low-dose irradiation. Low-dose irradiation does not produce any detectable change in the levels of volatile carbonyl compounds; irradiation at 8 kGy results in a transient increase in the total volatile compounds during subsequent storage in ice, but the increase is higher in the unirradiated shrimp. Radiation-induced changes in the fatty acid composition of shrimp are small. Some minor changes in the amino acid composition occur in irradiated shrimp; similar changes occur due to other processes such as canning and drying in hot air. Some vitamins in shrimp such as thiamine are affected by irradiation. But the loss is less extensive than in thermally processed shrimp. The protein efficiency ratio is not affected by irradiation of shrimp, and no adverse effects attributed to irradiation were found in animal feeding studies.

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CONTENTS

1. INTRODUCTION

Ionizing radiation is capable of inactivating microorganisms without appreciably raising the temperature. This makes ionizing radiation especially suitable for inactivating harmful and spoilage organisms in fresh and frozen commodities, and to preserve their fresh quality. As a result there has been considerable interest in the radiation preservation of these foods. Seafoods have received special attention because they are not only very nutritious but also highly perishable. There is a large body of literature on the radiation preservation of food from aquatic animals (see review by Nickerson et al., 1983; Licciardello and Ronsivalli, 1982) and various potential applications have been identified (Table 1), each with specific objectives.

The objective of radiation sterilization (radappertization) is to produce seafoods equivalent to conventional canned foods in microbiological safety. Such products can be stored at ambient temperatures without spoiling, and the probability of botulinum hazard is extremely low. Radiation processing of seafoods for shelf-stable products involves heat treatment to inactivate the enzymes prior to irradiation at a recommended dose of 30 to 40 kGy. Although the product is intended to be stored at ambient temperature, irradiation has to be carried out at sub-freezing temperatures. Little radappertization is done commercially at the present time.

Radurization or radiation pasteurization of seafoods takes advantage of the fact that most of the spoilage organisms are relatively sensitive to radiation. Therefore, low-dose irradiation can be used to selectively inactivate most of the spoilage organisms and so extend the shelf life. Normally the product still needs to be refrigerated.

The primary objective of radicidation is to reduce or inactivate non-spore-forming pathogenic microorganisms in food. However, the dose requirement is usually higher than that for radurization, and therefore the shelf life of the product is extended as well. Some seafoods such as shrimp develop radiation off-odor at doses over 1.5 kGy (Kumta et al., 1970; Roy and Kaylor, 1975; Angel et al., 1986) when irradiated at temperatures above freezing. Off-flavor results from the interaction of some food components with free radicals generated by radiation. Therefore, radicidation is carried out with the seafood in the frozen state. Thus, Wills (1981) decontaminated frozen shrimp at 6 to 8 kGy without any adverse effect on sensory quality. Wongchida et al. (1985) used 2 and 4 kGy to irradiate frozen shrimp and did not report any off-odor.

The effective use of any processing method, including radiation, depends on the microbiological quality of the starting materials. Heavily contaminated shrimp is likely to have a poor organoleptic quality in the first place because of decomposition caused by bacterial and autolytic enzymes. Neither irradiation nor any other process can improve the quality of such a product. Although high radiation doses can eliminate or reduce the microbial load, they cannot reverse the decomposition that has already taken place. And off-odor due to too much radiation is likely to aggravate the organoleptic quality even further. Therefore, good manufacturing/processing practices must be followed when shrimp are irradiated just as they would be in any other type of processing.

Shrimp and prawns (larger shrimp) are valuable commodities, especially in international trade. For example, Canada imported 1 182 744 kg of frozen shrimp in the inspection year 1986/87 (Fisheries and Oceans, 1987). A substantial fraction (7.4%) of this product was rejected for microbiological and other reasons. The rejected lots were either incinerated or returned to the shipper. Irradiation processing techniques have the potential to prevent such losses. Two large lots of frozen shrimp imported by Australia were successfully treated by irradiation and sold (Wills, 1981). The shrimp were irradiated to meet new microbiological standards that had been imposed without notice in Australia in 1978; the shrimp met the earlier standards that had been in effect previously. To date, irradiation of a variety of foods has been approved by 32 countries (Josephson and Brynjolfsson, 1987). Holland proposed mandatory irradiation of shrimp in the wake of 14 deaths due to consumption of contaminated shrimp (Swientek, 1985). Irradiated foods are being consumed in many countries (Anonymous, 1986). Canada allows a limited number of food items to be irradiated. There is a need to increase the use of this process to alleviate microbiological problems in other foods such as seafoods, meats and poultry.

This report reviews and summarizes the literature on the chemical effects of radiation on frozen and fresh shrimp.

2. EFFECTS OF RADIATION ON CAROTENOID PIGMENTS

The effects of radiation on the carotenoid pigments of shrimp are important from sensory and nutritional points of view. Shrimp have various characteristic shades of orange, red or pink color. These colors are essential components of sensory quality that undoubtedly is the dominant factor in consumer appeal. Carotenoid pigments that impart color to some fish and crustaceans occur widely in nature. They are found in bacteria, yeasts, molds, green plants and many animals (Simpson, 1982). Like other animals, shrimp and prawns cannot synthesize these pigments. They ingest the pigments with food and often modify them to their characteristic composition. Figure 1 shows the conversions of β-carotene to astaxanthin postulated to occur in shrimp. Some of the carotenoids, e.g., β-carotene, are precursors of vitamin A while others do not have any nutritional value.

Ionizing radiation degrades β-carotene and astaxanthin when they are irradiated in the pure form. Esters are more stable than the free astaxanthin (Table 2). However, pigments bound to shrimp protein in a complex environment behave differently. Snauwaert et al. (1973) showed that gamma irradiation up to 3 kGy did not significantly change the carotenoid pigments in cooked shell-on frozen brown shrimp (*Crangon vulgaris*). Kumta and Sreenivasan (1966) irradiated fresh shrimp at 1.5 to 10.0 kGy and found that radiation doses up to 2.5 kGy did not change the color of either the raw or the cooked shrimp (Table 3). At higher doses, a reddish colour appeared in the raw shrimp and faded to some extent with cooking. Lukton and MacKinney (1956) found that extractable astaxanthine of raw and cooked shrimp homogenate decreased only at very high radiation doses. Wills (1981) found no effect on the pigment following irradiation of frozen shrimp at 6 and 8 kGy.

Shrimp pigments are also highly sensitive to dehydration at the moderately high temperatures used by the processing industry. Table 4 shows the carotenoid composition in shrimp before and after drying at 70°C for 12 h. Carotenoid pigments are sensitive to oxidative changes due to the presence of conjugated double bonds. Oxidation results in the formation of epoxides, furanoids and other products (Davies, 1965).

Degradation of carotenoid pigments can also occur in the presence of lipoxygenase-type enzymes (Tsukuda and Amano, 1966,1967,1968) or by strong light (Simpson, 1982). Such degradation is inhibited by reducing agents.

The above reports suggest that irradiation of shrimp at temperatures above freezing and at doses over 2.5 kGy causes some loss of pigment color. Frozen shrimp may be irradiated at doses up to 8 kGy without appreciable loss of the pigment (Wills, 1981). Moreover, pigment loss is not unique to radiation processing.

3. EFFECTS OF RADIATION ON DEVELOPMENT OF BLACK SPOT (MELANOSIS) IN SHRIMP

Black spot is an undesirable development during storage of shrimp and this section deals with reports on the influence of radiation on melanosis.

Melanosis is the development of dark or brown pigmentation in shrimp and other crustaceans. It is a complex process involving the degradation of tyrosine by the phenolase type of enzymes. In shrimp these enzymes are concentrated primarily at the joints between segments of shell and are sensitive to irradiation (Novak et al., 1967). Melanosis can be prevented by chemical preservatives, e.g., potassium metabisulphite (Establier, 1968).

The effects of radiation on melanosis in shrimp are not well understood. Radiation of freshly caught shrimp reduced melanosis during subsequent refrigerated storage, but it accelerated melanosis in shrimp that underwent post-harvest storage prior to irradiation. It was hypothesized that phenolase products in aged shrimp bind to the enzyme to protect it from radiation damage and act as competitive inhibitors. After irradiation, the phenolase products lose their capacity to inhibit phenolase reactions, and act to protect the enzyme against radiation. The absence of such products in the freshly caught shrimp leads to the inactivation of the enzyme by radiation, and a subsequent reduction of melanosis (Urbain, 1986a).

Savagaon and Sreenivasan's (1975) observations were different for melanosis; melanosis was seen in Indian shrimp and lobster even when they were irradiated in extremely fresh condition. The authors demonstrated that irradiation caused the inactive precursor of the enzyme phenoloxidase in lobster shell to become active during subsequent storage. Radiation also increased the rate of release of tyrosine, the substrate for this enzyme in the lobster. Savagaon and Sreenivasan also found that the acti-

vity of the phenoloxidase enzyme was reduced considerably following irradiation. In view of these findings, the authors justify that the higher availability of tyrosine in the aged shrimp accelerated the reaction rate after irradiation, resulting in a net increase in the overall phenolase activity. The differences in the observations by Urbain (1986a) and by Savagaon and Sreenivasan (1975) on the influence of radiation on shrimp melanosis may also be due to different species of shrimp.

There are other reports showing that irradiation does not control melanosis (Hannesson and Dagbjartsson, 1972; Roy and Kaylor, 1975) in fresh shrimp. According to Urbain (1986a), blanching effectively prevents melanosis.

Irradiation of some species of raw shrimp may enhance the development of melanosis during subsequent storage and this may be controlled by heat treatment, chemical preservatives or by irradiating the raw shrimp immediately after harvest.

4. CHEMICAL TESTS USED TO EVALUATE IRRADIATED SHRIMP

This section discusses reports on the chemical tests used to evaluate the irradiated shrimp. Post-mortem changes brought about by autolytic enzymes and spoilage organisms generate a variety of compounds. The mechanisms involved in the formation of these compounds have been elucidated by a number of authors (Arai, 1966; Finne, 1982; Hebard et al., 1982, and Eitenmiller et al., 1982). The levels of these compounds are taken as the quality indices of shrimp and fish processed by irradiation and other methods. The following discussion examines how these tests can be correlated with the quality of irradiated shrimp on the basis of sensory scores.

Van Cleemput et al. (1980) irradiated deep-frozen blocks of tropical shrimp at 5 kGy and achieved a shelf life of 8 days at 6°C against 4 days for the unirradiated samples. The total volatile nitrogen (TVN) content increased with storage, with the increase being faster in unirradiated than in irradiated samples. Kumta et al. (1970) extended the shelf life of peeled fresh shrimp by irradiating them at 1.5 and 2.5 kGy up to 20 and 28 days, respectively, at 2 to 4°C, whereas the unirradiated shrimp had a shelf life of only 7 days. The increase in TVN and trimethylamine (TMA) levels was much slower in the irradiated than in the unirradiated shrimp during storage.

Vyncke et al. (1976) irradiated peeled, boiled brown shrimp at 1 kGy in 0.05- and 0.1-mm thick polyethylene pouches. The unirradiated shrimp in 0.05- and 0.1-mm thick bags had a shelf life of 9 and 16 days, respectively, whereas the irradiated shrimp under the same conditions kept for 23 ($\pm$2) days regardless of the type of packaging. Organoleptic results showed reasonable agreement with indices of spoilage consisting of TVN, ammonia, dimethylamine (DMA) and volatile acid number (VAN). There was no significant change in the TMA level in the irradiated shrimp during storage even after spoilage. There was practically no formation of hypoxanthine, TMA or volatile acids in the irradiated shrimp. Figure 2 shows the sensory scores for the treated and untreated shrimps as a function of storage time as well as the levels of various chemical indices.

Earlier, Vyncke and Declerck (1972) investigated the effects of radiation doses on the shelf life of cooked whole brown shrimp packed in polyethylene bags. They found that the shrimp irradiated at 0.5 kGy was acceptable for up to 19 (±2) days. Of the chemical indices, TVN, ammonia, hypoxanthine and DMA correlated best with organoleptic scores (Figure 3). The free amino acid level and redox potential values remained practically unchanged for the irradiated shrimp, but dropped significantly for the unirradiated samples during storage, indicating microbiological activity.

Liuzzo et al. (1970) irradiated fresh headless shell-on gulf shrimp at 0.5, 1.0 and 2.5 kGy to extend their shelf life during storage in ice. Chemical and organoleptic analyses showed that as the organoleptic scores declined during a six-week storage study, the pH increased, and ammonia and TMA levels rose significantly faster in the unirradiated samples than in the irradiated ones. Houwing et al. (1978) examined the effects of irradiation and of 0.4% benzoic acid on the shelf life and chemical and organoleptic qualities of Dutch shrimp. The shelf life of the peeled shrimp treated with irradiation alone (1 kGy) doubled, and that of shrimp treated with 0.4% benzoic acid tripled compared to that of the untreated shrimp. In the case of unpeeled shrimp, irradiation enhanced shelf life by a factor of 3, and 0.4% benzoic acid treatment by 2.7. The authors also determined the average content of chemical spoilage products (Table 5) towards the end of the useful shelf life. They found practically no difference in ammonia, TMA and hypoxanthine levels between irradiated and unirradiated peeled shrimp. However, in the unpeeled shrimp there were significantly lower levels of these indices in the irradiated samples than in the unirradiated samples.

Nouchpramool et al. (1983) irradiated raw frozen peeled and headless shell-on shrimp (*Penaeus merquiensis*) at 2 and 4 kGy that were then stored at -18°C for 7 months. Both irradiated and unirradiated shrimp were found organoleptically acceptable. The pH of the irradiated and the unirradiated samples rose slightly during storage, presumably due to breakdown of nitrogenous muscle components. The TMA levels of frozen unirradiated and irradiated peeled and shell-on headless shrimp were very low and fluctuated during the 7-month storage period. TVN values of headless shell-on shrimp were somewhat higher, especially at the beginning, than those of the peeled shrimp. Again, there were fluctuations in the TVN levels during storage of treated and untreated shrimp. There was a slight increase in the TBA values of the shrimp after irradiation, but the levels dropped during storage. The authors did not find any correlation between organoleptic scores and any of these chemical tests.

Scholz et al. (1962) irradiated vacuum-packed frozen shrimp meat at 5 and 7.5 kGy, and examined their sensory and chemical indices during 18 weeks of storage at 0 and 38°F.* The pH of the unirradiated shrimp stored at 38°F rose from 7.43 to 7.98, whereas there was very little change in the pH values of the irradiated shrimp. TVN, TMA and VAN levels of irradiated shrimp changed slightly during 18 weeks of storage at 38°F. The irradiated samples had somewhat lower preference scores compared to the unirradiated ones at the initial stage due to radiation off-flavor, but both the unirradiated samples held at 0°F and 38°F had comparable scores up to 3 weeks.

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* $^{0}C = (^{0}F - 32)/1.8$

The authors did not establish any correlation between sensory scores and chemical indices, presumably because of complications due to radiation off-odor. A later report from the same laboratory (Awad et al., 1965) presented irradiation results for frozen whole shrimp (*P. setiferous*) and evaluated its chemical and sensory qualities during 10 weeks of storage at 38°F. During storage the pH values of the flesh and drip of unirradiated shrimp rose significantly, whereas there was very slight change in the pH values of irradiated samples. TMA and TVN values of the unirradiated shrimp stored at 38°F for 1 week were either equal to or higher than those of the irradiated shrimp after 10 weeks of storage. The indole content of unirradiated sample was initially 4.0 µg/100 g, but rose to 16.8 µg/100 g in one week of storage at 38°F. On the other hand, the level of indole in the irradiated shrimp fluctuated during storage between 2.9 and 8.0 µg/100 g. The irradiated shrimp showed somewhat lower preference scores than the unirradiated frozen shrimp throughout the storage period.

Irradiation effectively arrests spoilage of shrimp and in most cases chemical tests correlate well with sensory scores for shrimp stored in ice or at refrigeration temperatures. These tests are of limited use for irradiated shrimp stored frozen.

5. GAS CHROMATOGRAPHIC ANALYSES OF TRACE VOLATILE COMPOUNDS

Volatile carbonyls occur naturally in fish and crustaceans, and they may be formed by bacterial action, radiolysis or pyrolysis (Ismail, 1971). They are usually monocarbonyls, but often there may be an additional functional group whose chain length usually does not exceed 10 carbon atoms. These compounds are extracted by various methods including vacuum or steam distillation, and aeration. They are separated, identified and quantitied by gas chromatography. The objective of analyzing the volatile carbonyls is to understand their role in food flavor and how processing affects them (Flick et al., 1982), and their possible toxicological effects (Brynjolfsson, 1981).

Novak and Liuzzo (1964) reported the isolation and gas chromatographic analyses of volatile carbonyl and amino compounds from fresh shrimp irradiated at 1.5 kGy. They found the same compounds in both irradiated and unirradiated samples, except acetone, which was found only in the unirradiated sample (Table 6). In general, irradiated shrimp had lower amounts of the volatiles than the unirradiated sample except 2,4-pentadione, 2-hexanal, 2-octanal, methylamine and ethylamine, which were higher in the irradiated sample. Direct gas chromatographic/mass spectrometric analysis of total volatile compounds (Rayner et al., 1981) in previously frozen unirradiated shrimp stored at 4°C showed a profile somewhat different from that reported by Novak and Liuzzo (1964): they found methanol, methanethiol, ethanol, dimethyl sulphide, acetone, trimethylamine, methylpyridine, and indole. The levels of these compounds increased during storage for 14 days (Rayner et al., 1981). The difference in the results for unirradiated shrimp reported by Novak and Liuzzo (1964) and by Rayner et al. (1981) is most likely due to difference in the analysis methods.

Ismail (1971) identified eleven different carbonyls in fresh and irradiated shrimp immediately after irradiation as well as at various times during storage in ice for up to 30 days. The level of total volatiles in the shrimp irradiated at 8 kGy was higher than in the unirradiated shrimp. The level increased, reaching its peak on day 7, and then declined (Figure 4). The level in the control increased to a much higher level than in the irradiated sample, but rather slowly, and then declined. On the thirtieth day of storage, the control sample had a higher total carbonyl level than any of the irradiated samples. The level of total carbonyls in the shrimp irradiated at 1.5 kGy was initially about the same as that of the control, and did not change significantly during the 30-day storage in ice.

When the carbonyls were separated by gas chromatography, Ismail (1971) observed that acetaldehyde and propionaldehyde were the major components of the volatile carbonyls. Acetone + isobutaraldehyde, diacetyl and 2-heptanone levels were moderate; there were traces of hexanal and butanone (Table 7). Following irradiation at 8 kGy, the levels of propionaldehyde, butaraldehyde, diacetyl and 2-heptanone + heptaldehyde increased somewhat, but the author did not consider the increase to be significant. There were no changes in the levels of the other carbonyls. Changes in the levels of some of the individual carbonyls while the shrimp were stored on ice (shown in Tables 8, 9 and 10) are in general agreement with the patterns shown in Figure 4, i.e., there was an initial increase in carbonyls during storage followed by a decrease. Two unknown components were detected in trace quantities in the shrimp irradiated at 8 kGy (Table 10).

Ronsivalli et al. (1971) reported the presence of volatile compounds while they were using gas chromotography to analyze the headspace gas from irradiated cod and haddock fillets. The irradiation doses were 2, 28 and 56 kGy, and the fillets were stored at 4.4°C before analysis. The identity of the compounds in the chromatograms was not reported. However, the authors concluded that the general effect of irradiation was to increase the number and size of the peaks associated with the volatile compounds. The effects were similar when the unirradiated samples were stored at 4.4°C. The temperature of the sample during irradiation was not specified for the 2-kGy samples, but King et al. (1972) reported later that the irradiation at 28 and 56 kGy was carried out at ambient temperatures, which are not appropriate conditions for radappertization because of the extremely high levels of volatile radiolytic products formed at high doses at ambient temperatures (Merritt et al., 1978).

Gadbois et al. (1967) identified sixteen different volatile carbonyls in clam meat. The levels of these componds increased either when the shrimp were irradiated at 4.5 kGy or stored in air at 33-35°F. The levels of the compounds in the irradiated shrimp decreased with further storage. Radiation did not induce the formation of any new carbonyl compounds, but only accelerated the formation and dissipation of these compounds. Cooking decreased the levels of the more volatile components in both irradiated and unirradiated samples.

The reports discussed above indicate that irradiation of shrimp at 1.5 kGy does not produce any new volatile compounds. During storage, the level of total volatile carbonyls is less in the irradiated than in the

unirradiated shrimp. Irradiation at 8 kGy followed by storage resulted in a transient increase in the level of total volatile carbonyls, but the increase was less than in the unirradiated shrimp.

6. EFFECTS OF RADIATION ON THE PROXIMATE COMPOSITION OF SHRIMP

This section deals with natural variations in the composition of shrimp and how they are influenced by radiation and other processes.

The composition of shrimp varies with the species, age and harvest season (Shaikhmahmud and Magar, 1961; Doughlin and Teeri, 1960; Gopalakrishnan, 1951; Shaikmahmud and Magar, 1957; Dabrowski et al., 1969; and Gallagher and Brown, 1975). The yield of shrimp meat varies with size; larger shrimp usually yield more meat on a weight percent basis than smaller shrimp. Dabrowski et al. (1969) found the meat yield to range from 47.2 to 55.1% in an analysis of a large number of shrimp ranging from 15.5 to 23.4 cm in length. The average yield was 51.3%.

The approximate composition of eight species of prawns from the Indian Ocean is presented in Table 11. As in any other muscle foods, water is the main component of prawns. Of the total solid content, protein is the major component, and fat is one of the minor components.

Reber and Bert (1968) analyzed the protein, fat, moisture, fiber and ash contents of fresh irradiated (1.5 and 3.0 kGy) and of cooked unirradiated shrimp (*P. setiferous*). After the irradiated and cooked samples were stored in ice for 30 days, the protein, fat, and ash content of the irradiated samples remained virtually the same as that of the unirradiated frozen control. The cooked sample showed slightly lower protein and much higher ash content than the control. The authors did not examine the effects of cooking on the nutrient content of the shrimp after they had been irradiated and stored.

Srinivas et al. (1974) reported the nutrient content of shrimp meat under various processing conditions, namely canning, freeze drying, partial drying of blanched shrimp (to 40% moisture by hot air at 55 to 60°C), air drying (65 to 70°C for 8 to 10 hours) as well as irradiation (2.5 to 3.2 kGy) of the partially dry shrimp packed in various atmospheres. The proximate composition of the shrimp under various conditions is shown in Table 12. Blanching prior to canning or partial dehydration led to about a 7% reduction in the protein content compared with the fresh shrimp meat. The authors attributed this to the loss of water-soluble nitrogenous materials in the water. However, the sum of the percentages of the components of the canned and partially dry shrimp was less than 100%, and the authors did not offer an explanation for this discrepancy. Nonetheless, a comparison of the data for partially dehydrated shrimp with data for irradiated shrimp suggests that irradiation does not affect the protein, fat and mineral content in a significant way.

It is obvious from these reports that low-dose irradiation does not cause any detectable change in the proximate composition of shrimp.

7. EFFECTS OF IRRADIATION ON PROTEINS AND AMINO ACIDS IN SHRIMP

Shrimp and other foods of animal origin are the best protein sources, and so any radiation effects on them are of utmost importance. The chemical consequences of irradiating protein in model systems and in foods has been examined by many authors (Merritt and Taub, 1983; Urbain, 1986b; Lakritz et al., 1987). Merritt et al. (1966) observed that irradiation (60 kGy) of defatted chicken meat and haddock muscle (0.3% fat) yielded mainly aromatic hydrocarbons (benzene and toluene) and sulfur compounds (methyl mercaptan and dimethyl sulphide) as well as some other minor compounds, e.g., ethylbenzene, ethylmercaptan, methane, carbonyl sulfide, and hydrogen sulfide.

The authors also examined the radiolysis of several amino acids, and concluded that the major effect on amino acids is decarboxylation. Other products are derived from the likely cleavage of the side chains. Thus, hydrogen sulfide and dimethyl sulphide are the likely derivatives of cystine and cysteine, respectively. Toluene was derived from phenylalanine.

Liuzzo et al. (1970) found that homogenate from shrimp irradiated (2 kGy) and then cooked had a higher viscosity than the homogenate from shrimp samples that were only cooked. This is probably due to radiation-induced aggregation of protein (Kraybill, 1984). Novak and Liuzzo (1964) found little irradiation effect on the solubility of shrimp protein (Table 13).

Shewbart et al. (1972) detected 19 amino acids in brown shrimp (*P. aztecus*) from the Gulf of Mexico; 11 of these amino acids were essential. The essential amino acid pattern resembled that of most other members of the animal kingdom, which indicates the high quality of shrimp protein. Srinivas et al. (1974) compared the total amino acid composition of Indian shrimp processed by irradiation and other methods. Table 14 shows that irradiation (2.5 to 3.2 kGy) of partially dehydrated shrimp (40% moisture) at ambient temperature resulted in a very slight (less than 5%) reduction of some of the amino acids, namely alanine, isoleucine, leucine, and tyrosine, whereas there was a slight increase in the level of half cystine (5.8%) compared with the corresponding levels of amino acids in the unirradiated shrimp. There were similar changes in the levels of some of the amino acids in the canned shrimp as well. Air drying at 65 to 75°C caused up to an 8% loss of some of the essential amino acids.

Yeh and Hau (1988) determined the total amino acid composition of grass shrimp (*Penaeus monodon*) irradiated at doses up to 100 kGy at -10°C. The only noticeable change was the increase of valine in the irradiated shrimp compared with the unirradiated shrimp (Table 15), and is probably due to experimental error. The levels of cystein, cystine, and tryptophan were not reported for any of the samples.

Vervack et al. (1977) compared the total amino acid composition of Belgium shrimp (*Crangon vulgaris*) processed by irradiation and other methods. They found that the mean percentages of threonine, glutamic acid, methionine, isoleucine, leucine, and available lysine in the irradiated

samples were lower (6.7 to 23.5%) than in the fresh shrimp. On the other hand, the percentages of aspartic acid and proline were higher in the irradiated samples than in the fresh sample by 35% and 14%, respectively. Similar changes were reported for some amino acids in frozen and canned shrimp. It should be noted that the report did not provide any information as to the conditions used in processing the shrimp, namely radiation dose, temperature, etc., which are important factors in chemical changes in foods. Therefore, no meaningful conclusion can be drawn from this report.

Tryptophan, an essential amino acid for humans, is limiting in shrimp. Antunes and Novak (1978) examined the tryptophan-protein ratio (g tryptophan/100 g protein) in shrimp (*P. setiferous*) irradiated at 2, 10, and 45 kGy at -2, 39, and 80°F in frozen as well as freeze-dried form. The decreases in the tryptophan-protein ratios due to irradiation were very small (1.5 to 1.86%).

The available lysine content (lysine residue in protein with the epsilon amino group free) is considered an important quality index for foods. Both irradiation and heat treatment may affect the available lysine content in some protein foods (Ford and Salter, 1966; Vervack et al., 1977). Srinivas et al. (1974) observed no change in the available lysine in partially dehydrated shrimp when irradiated (2.5 to 3.2 kGy) at ambient temperature, whereas drying in hot air (65 to 70°C) resulted in slightly less available lysine.

Srinivas et al. found a slight increase in the *in vitro* digestibility of irradiated shrimp protein by pepsin and trypsin, compared with unirradiated shrimp (Figure 5).

Free amino acids are important elements of seafood flavor, and irradiation increases the level of free amino acids (King et al., 1972). Gamma irradiation caused up to an 8% increase in some of the free amino acids in partially dehydrated shrimp (Srinivas et al., 1974).

The reports that provide detailed processing information indicate that irradiation of shrimp causes a small decrease in the levels of some of its amino acids, while there is some increase in the levels of others. Changes due to radiation are less than those due to air drying and canning.

8. EFFECTS OF IRRADIATION ON SHRIMP LIPIDS

Our present knowledge of the radiation chemistry of lipids comes from the irradiation of fatty foods and from model systems consisting of simple compounds, e.g., free fatty acids, methyl esters and triglycerides. The radiolytic changes in each of these systems followed similar mechanisms such as decarboxylation, dehydrogenation, polymerization and cleavage of the alkyl chain. The relative proportions of the various compounds formed in a given system vary with temperature, radiation dose, the presence of oxygen and the nature of the starting materials (Vajdi et al., 1982; Nawar, 1978). The major end products of fatty acids are CO_2, CO, H_2, hydrocarbons, e.g., alkanes, alkenes and aldehydes. Dimers and polymers can form with the unsaturated fatty acids. Propanediol diesters are formed from glycerol.

Relatively little is known about the radiation effects on phospholipids (Urbain, 1986b). Lecithin yields fatty acids and choline phosphate. When DL-γ-dipalmitoyl phosphatidyl ethanolamine is irradiated at a very high dose (500 kGy), it yields hydrocarbons, alkanals, alkanones, esters, palmitic acid, palmitone, lysophosphatidyl ethanolamine, and ethanolamine phosphate. Radiolytic cholesterol products include the hydrocarbons derived from the side chain and cholestane-3β:5α:6β triol.

Studies on the radiation chemistry of food lipids have concentrated primarily on isolated lipids or lipid-containing tissues of fatty species, e.g., beef, mutton, lamb, veal, pork and poultry (Merritt, 1972; Merritt et al., 1978; Gruiz and Kiss, 1987; and Delincee, 1983). Relatively little is known about the radiation chemistry of lipids in lean marine species (King et al., 1972).

Lipids from cod and haddock muscles (Ronsivalli et al., 1971) and marine shrimp (Gopakumar and Nair, 1975) contain a high proportion of phospholipids and small proportions of triglycerides, compared to fatty species, e.g., chicken, beef, etc., where triglycerides form the major component.

Table 16 shows the composition of the lipid classes in Indian prawns. Phospholipids are the major lipids in these prawns. A species of freshwater prawn has been reported to contain more triglycerides (Chanmugan et al., 1983) in its lipids than phospholipids. The fatty acid pattern of five different species of shrimp is shown in Table 17, and the fatty acid pattern of different types of lipids of a marine and a freshwater species are compared in Table 18. These tables show that shrimp lipids are rich in polyunsaturated fatty acids, which are susceptible to radiolysis (King et al., 1972).

Information on the effect of radiation on shrimp lipids is limited. Novak and Liuzzo (1964) reported the gas chromatographic analysis of the volatile free fatty acids isolated from shrimp irradiated in fresh condition at 1.5 kGy. As shown in Table 19, fatty acids in irradiated shrimp were also found in the unirradiated samples. These data on free fatty acids clearly show there is no qualitative difference between the free fatty acid composition of irradiated and unirradiated shrimp. However, the analysis involved hydrogenating the isolated fatty acids prior to gas chromatography and so did not show the unsaturated fatty acids except $C_{22:1}$. Moreover, the total fatty acid composition of the shrimp was not shown in the report.

A somewhat more detailed analysis of irradiated shrimp was reported by Ismail (1971). She analyzed the total fatty acid composition of unirradiated and irradiated (1.5 and 8 kGy) shrimp after storage in ice for up to 24 days. The only noticeable difference between the irradiated and unirradiated shrimp on the first day was a drop in the level of palmitic acid at 1.5 kGy, but there was no significant difference in the palmitic acid level between the unirradiated shrimp and shrimp irradiated at 8 kGy (Table 20). One would expect the level of some of the unsaturated fatty acids to drop because they are highly reactive (King et al., 1972). But Ismail found no noticeable difference in the levels of the unsaturated fatty acids between irradiated and unirradiated samples. In fact, some of

the high-molecular-weight free fatty acids (C_{22}) reported by Novak and Liuzzo (1964) were not reported by Ismail (1971). Ismail did not specify either the sample size or the units for the fatty acid values in the table.

Yeh and Hau (1988) irradiated frozen (-10°C) headless grass shrimp at doses up to 100 kGy and found little effect on the composition of the long-chain fatty acid of the shrimp, as shown in Table 21. At 2.5 kGy, the percentage of stearic acid ($C_{18:0}$) dropped (11.5%) and that of oleic acid ($C_{18:1}$) increased (8.3%) compared with the levels present in the unirradiated sample. The linoleic acid level ($C_{18:2}$) decreased somewhat in the sample irradiated at 100 kGy, while the percentages of palmitic and stearic acids increased. These changes do not appear to be proportional to dose and are probably due to experimental variations.

Ronsivalli et al. (1971) reported some drop in the levels of some of the polyunsaturated fatty acids in cod and haddock fillets irradiated at 28 and 56 kGy, presumably because of a radiation-induced increase in oxidation (King et al., 1972). There was no decrease in the levels of unsaturated fatty acids in the fish irradiated at 2 kGy. Small amounts of three unidentified compounds were detected in the lipid extracts from cod and haddock fillets irradiated at 28 and 56 kGy. These compounds were not detected in the lipid extracts from unirradiated and low-dose (2 kGy) irradiated fillets. It is worth noting that the high-dose (28 and 56 kGy) irradiation was carried out at ambient temperatures, which are not appropriate for irradiation of muscle foods.

Novak and Liuzzo (1964) determined the cholesterol levels in irradiated and unirradiated shrimp. Data shown in Table 22 show that there is probably no significant radiation effect on the cholesterol level in shrimp.

Despite the fact that shrimp lipids contain a high proportion of unsaturated fatty acids, the data indicate that irradiation of shrimp results in small changes in its fatty acid pattern. The effect on cholesterol level is insignificant. This is consistent with the fact that lipids comprise only a very small fraction of shrimp, and therefore are expected to be protected against radiation-induced changes by other components.

9. EFFECTS OF RADIATION ON SHRIMP CARBOHYDRATES

Radiation-induced reactions in carbohydrates include changes in the melting point, optical rotation, formation of various gases, e.g., H_2, CO_2, CH_4, and CO, degradation of glycosidic bonds, and formation of acids and aldehydes; these reactions were established in model studies. Some of these changes are due to the direct effects of radiation and others are due to the interaction of free radicals generated by radiolysis of water with carbohydrates. The presence of other food components such as proteins and lipids provides protection against these changes (Urbain, 1986b).

Carbohydrates are a very minor component of shrimp meat. Shaikhmahmud and Magar (1961) reported that the glycogen content varied from 213 to 435 mg/100 g of muscle on a dry-weight basis, and the fiber content of

San Francisco Bay brine shrimp was calculated to be 3.5% (Gallagher and Brown, 1975). There is little information on the chemistry of carbohydrates in irradiated shrimp. Model studies (Saini, 1968) suggest that there would be some degradation of the polysaccharides, e.g., glycogen, but no significant increase of soluble sugar or decrease of glycogen content was observed (Liuzzo et al., 1970) in oysters irradiated up to 4 kGy and stored in ice for up to 20 days. This is consistent with the view that other components present in the shellfish had protective effects on the carbohydrates.

As in oysters, carbohydrates are a minor component of shrimp and are probably not affected by irradiation to any significant extent.

10. EFFECTS OF RADIATION ON VITAMINS IN SHRIMP

Radiation causes a loss of some vitamins, depending on the radiation dose and other conditions; the loss is much higher in simple solutions than in the complex environment in foods. For example, Urbain (1986b) stated that only a small loss of vitamin C occurred when fruits and vegetables were irradiated up to 5 kGy. The loss of thiamine was substantial in minced beef irradiated at 10 kGy, but the loss was reduced when the beef was irradiated frozen.

Radiation effects on the levels of some B vitamins in partially dehydrated shrimp were reported by Srinivas et al. (1974). As shown in Table 23, blanching and partial dehydration (40% moisture level) at 55 to 60°C led to losses of 36 to 59% of some B vitamins. Following irradiation at 2.5 to 3.2 kGy, the losses ranged from 8 to 18.5%, except for thiamine which showed a 35.5% loss. However, thiamine losses were minimized in samples irradiated in a vacuum or a nitrogen atmosphere. It is noteworthy that drying in the air (65 to 70°C) and canning (40 min at 70 kPa) led to losses higher than those due to irradiation. The vitamin content of the shrimp also decreased during storage after processing by irradiation or by other methods, as shown in Table 24. Thiamine and riboflavin losses were similar after storage for 3 months at ambient temperatures for products processed by various methods. Again, the losses were less in vacuum-packed samples and in those packed in a nitrogen atmosphere than for samples processed in presence of air.

Yeh and Hau (1988) measured the levels of thiamine and niacin in headless grass shrimp irradiated at various doses up to 50 kGy at -10°C. The loss of thiamine increased almost linearly with dose up to 10 kGy; above that dose, the additional loss was low. The niacin level also decreased linearly with dose up to 25 kGy and then leveled off. The authors reported that niacin and thiamine losses were 1.45 and 14.6%, respectively, following irradiation at 4.5 kGy (radiation off-odor occurred above this dose), a much lower loss than reported by Srinivas et al. (1974). This is consistent with reports (Wilson, 1959) that vitamin loss due to radiation is significantly influenced by the temperature at which the irradiation is carried out.

Brooke et al. (1964) investigated the effects of refrigerated storage, heat processing, and irradiation on the B-vitamin content of clam

meat. They showed that irradiation at 3.5 and 4.5 kGy and steaming for 15 minutes did not significantly change the levels of riboflavin, thiamine and niacin. There was a moderate drop in the levels of pyridoxin when clam meat was irradiated at 4.5 and 45 kGy, and stored at 33°F for 30 days. Heat processing (20 minutes at 240°F) slightly decreased the levels of niacin and vitamin B_{12}.

Radiation causes various types of reactions in vitamin A in lipid solvents, depending on whether vitamin A is present as acetate or alcohol. In foods, the radiation sensitivity of the vitamin depends on composition; certain carbohydrates, proteins, ascorbic acid and α-tocopherol provide protection to vitamin A or its precursor β-carotene (Urbain, 1986b). Miller et al. (1958) reported a 55% loss of vitamin A in butter irradiated at 2.4 kGy. Under the same conditions, margarine lost only 9%. Irradiation of salmon at 2 or 5 kGy led to severe damage of its carotenoids (Miller et al., 1958).

Vitamin A levels in shrimp have been variously reported as 25 IU (Osborne and Voogt, 1978) and 73.3 IU (Gordon and Martin, 1982) per 100 g. A much higher level (6650 IU/g) was reported by Gallagher and Brown (1975). The last figure is probably incorrect, although it is possible that the high level is due to a difference in species. Vitamin A activity is due to both β-carotene and vitamin A (Osborne and Voogt, 1978). None of the reports indicate how much of the vitamin A activity in shrimp is due to β-carotene. The amount of vitamin A in shrimp lost due to irradiation is not known, but carotene is only slightly destroyed in shrimp even at 18.6 kGy (Miller et al., 1958)

Very little is known about the types of products derived from vitamins as a result of food irradiation. This is not unexpected because food contains very small amounts of vitamins, and radiation degradation *in situ* is even smaller. It is likely that there are several degradation products from each vitamin, making measurements very difficult, if not impossible.

However, the lack of information in this area is not particularly serious because the extent of degradation is very small. Moreover, the nutritional contribution of shrimp to the Canadian diet is very small, because per capita annual consumption of shellfish is only of the order of a kilogram (Food and Agriculture Organization, 1979).

Irradiation of shrimp at ambient temperatures results in substantial losses of some vitamins. However, the losses due to radiation are less severe than those due to blanching, hot-air drying and canning. Losses are significantly less in shrimp irradiated in a vacuum, or in a nitrogen atmosphere, as well as in shrimp irradiated when frozen.

11. ANIMAL FEEDING TESTS

Animal feeding is the ultimate test for the quality of processed foods. Miller et al. (1958) reviewed the wholesomeness of irradiated seafoods including shrimp. Dogs and rats were fed diets containing up to 70%

irradiated seafood that had been exposed to 28 or 56 kGy of gamma rays. The animals were fed for up to three years and measurements included gross food utilization, growth, hematology, histopathology, reproduction and lactation through at least three generations in rats and one generation in dogs. There was no evidence of any abnormal responses that could be attributed to irradiated food.

A study conducted in the Netherlands (van Logten et al., 1972) involved feeding various diets for 90 days to seven groups, each containing 10 male and 10 female rats. The diet was either a standard diet or one of several containing non-irradiated and irradiated (1.5, 3.0 kGy) shrimp (up to 28% of the diet on dry basis). The growth, food intake, blood composition, serum glutamic-pyruvic transaminase, weights of organs and histopathology were followed. No adverse effects on these parameters were observed that could be attributed to irradiation. However, the relative weights of liver, kidneys and ovaries of the animals were affected when the diet contained 28% shrimp regardless of whether the shrimp was irradiated or not.

Aravindakshan et al. (1973) irradiated partially dehydrated (40% moisture) shrimp at 2.5 kGy and found that the product, when fed to rats of both sexes at 25% level in the diet for up to four generations, did not adversely affect growth, reproduction, lactation, longevity, organ histology and other biochemical characteristics.

Irradiation of shrimp does not affect its protein efficiency ratio determined by rat feeding tests (Reber and Bert, 1968; Srinivas et al., 1975).

The reports discussed here clearly show that the protein efficiency ratio is not affected by irradiation of shrimp. No adverse effects attributable to irradiated shrimp were observed in animal feeding tests.

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TABLE 1

RADIATION DOSES REQUIRED FOR VARIOUS APPLICATIONS OF THE RADIATION PRESERVATION OF SEAFOODS[a]

Process	Objective	Dose (kGy)
Radurization	Extension of shelf life	0.75-2.5
Radicidation	Inactivation of non-sporeforming pathogens	2.5-10.0
Insect disinfestation	Control of insects	1.0
Radappertization	Commercial sterility	30.0-40.0

[a] From Giddings (1984)

TABLE 2

INFLUENCE OF GAMMA-RAY IRRADIATION[1] ON ISOLATED SHRIMP PIGMENTS[a]

Pigment	Degradation %
Astaxanthin	69
Astaxanthin monoester	55
Astaxanthin diester	6

[1] 1.5 kGy
[a] From Declerck and Vyncke (1972)

TABLE 3

EFFECT OF IRRADIATION ON COLOR AND PIGMENT LOSS OF RAW AND COOKED SHRIMP

Dose (kGy)	Pigment Loss/Appearance		Reference
	RAW	COOKED	
1.5-2.5	Normal	Normal	Kumta and Sreenivasan (1966)
5.0	Normal	Slight fading of the red color	
7.5	Slight reddish tinge	Slight fading of the red color	
10.0	Reddish tinge	Marked fading of the red color	
0.0	0.0 %	9.5 %	Lukton and Mackinney (1956)[1]
9.3	44.5 %	33.6 %	
18.6	39.2 %	54.2 %	
37.2	58.3 %	58.0 %	

[1] Pigment was extracted from the treated and untreated shrimp and estimated spectrophotometrically. The figures indicate % loss compared with the value of the unirradiated shrimp extract.

TABLE 4

COMPOSITION OF CAROTENOIDS IN SHRIMP MEAL BEFORE AND AFTER DRYING[a]

Carotenoids	Before Drying (μg/g dry basis)	After Drying
3,3'-Dihydroxy-ε-carotene	1.36	
Echinenone	0.25	
Isocryptoxanthin	0.38	
Canthaxanthin	0.39	
4-Keto-4'-hydroxy-β-carotene	0.74	
Dihydroxypiradixanthin	4.66	
Lutein	trace	
Zeaxanthin	trace	
Astaxanthin ester	66.1	10.3
Astacene	55.4	6.26
Astaxanthin	7.19	trace

[a] From Simpson (1982)

TABLE 5

AVERAGE CONTENT OF CHEMICAL SPOILAGE PRODUCTS NEAR THE END OF USEFUL SHELF LIFE[a]

	Spoilage Products		
Treatment	TMA (mg % N)	Hypoxanthine (mg % N)	Ammonia (mg % N)
Peeled			
0 kGy + benzoic acid	1.7	2.2	31
0 kGy	4.1	12.0	29
1.0 kGy + benzoic acid	0.9	4.6	31
1.0 kGy	4.8	12.0	26
Unpeeled			
0 kGy + benzoic acid	2.6	11.0	28
0 kGy	10.6	18.0	40
1.0 kGy + benzoic acid	2.4	1.1	33
1.0 kGy	3.7	1.5	29

[a] From Houwing et al. (1978)

TABLE 6

QUANTITIES OF CARBONYL AND AMINES PRESENT

IN IRRADIATED (1.5 kGy) AND UNIRRADIATED SHRIMP[a]

(expressed in moles)[1]

Compound	Irradiated Shrimp	Unirradiated Shrimp
Acetaldehyde	0.010609	0.113940
Propinaldehyde	0.001271	0.004170
Isobutyraldehyde	0.000228	0.005733
N-butyraldehyde	0.000202	0.000613
2-methyl-1-pentaldehyde	0.00118	0.000121
2,4-pentadienal	0.000187	0.000305
2,4-pentadione	0.000164	0.000081
2-hexanal	0.000643	0.000554
2-octanal	0.000327	0.000920
Citronellal	0.000066	0.000292
Acetone	----	0.000320
Trimethylamine	0.0419	0.3074
Ammonia	0.1184	0.6985
Methylamine	2.8715	1.9099
Dimethylamine	0.0193	0.0604
Ethylamine	0.0717	0.0411
Propylamine	0.0128	0.0362
Butylamine	0.0192	0.0383

[1] Sample size not specified

[a] From Novak and Liuzzo (1964)

TABLE 7

EFFECTS OF IRRADIATION AT TWO DIFFERENT DOSE LEVELS

ON VOLATILE CARBONYLS IN SHRIMP[a]

Carbonyl Compounds	non-Irradiated	Irradiated at 1.5 kGy	Irradiated at 8 kGy
Acetaldedyde	+++	+++	+++
Propionaldehyde	++++	++++	+++++
Acetone			
Isobutyraldehyde	++	++	++
Butyraldehyde	+	++	+++
Butanone	Trace	Trace	+
3-Methyl-2-butanone			
Diacetyl	++	+++	+++++
Hexanal	Trace	Trace	Trace
2-Heptanone			
Heptaldehyde	++	+++	+++++

\+ Represents the smallest relative peak height
Trace: Represents a slight hump on chromatogram

[a] From Ismail (1971)

TABLE 8

CHANGES IN VOLATILE CARBONYL COMPOUNDS DURING ICE

STORAGE OF CONTROL NON-IRRADIATED SHRIMP[a]

Carbonyl	0.0 days	7 days	14 days	21 days	30 days
Acetaldehyde	+++	+++	++++	++++++	+++++
Propionaldehyde	++++	++++	+++++	++++++	+++++
Acetone					
Isobutyraldehyde	++	++	+++	++++	+++
Butyraldehyde	+	+	++++	++++	+++
2-Butanone	Trace	Trace	Trace	+	Trace
3-Methyl-2-butanone					
Diacetyl	++	++	+++++	++++++	++++
Hexanal	Trace	Trace	Trace	+	+
2-Heptanone					
Heptaldehyde	++	+++	++++	+++++	+++

\+ Represents the smallest relative peak height
Trace: Represents a slight hump

[a] From Ismail (1971)

TABLE 9

CHANGES IN VOLATILE CARBONYL COMPOUNDS DURING ICE STORAGE OF SHRIMP IRRADIATED AT 1.5 kGy[1]

Carbonyls Detected	0.0 days	7 days	14 days	21 days	30 days
Acetaldehyde	+++	+++	+++	+++	+++[a]
Propionaldehyde	++++	++++	++++	++++	++++[a]
Acetone					
Isobutyraldehyde	++	++	++	++	++[a]
Butyraldehyde	++	+	+	+	+[a]
2-Butanone	Trace	Trace	Trace	Trace	Trace
3-Methyl-2-butanone					
Diacetyl	+++	++	++	++	+++
Hexanal	Trace	Trace	Trace	Trace	Trace
2-Heptanone					
Heptaldehyde	+++	++	++	+++	+++

\+ Represents the smallest relative peak height
[a] Slightly less than the number of +
Trace: Represents a slight hump

[1] From Ismail (1971)

TABLE 10

CHANGES IN VOLATILE CARBONYL COMPOUNDS DURING ICE STORAGE ON SHRIMP IRRADIATED AT 8 kGy[a]

Carbonyl	0.0 days	7 days	14 days	21 days	30 days
Acetaldehyde	++++	+++++	+++++*	++++	++++*
Propionaldehyde	+++++	++++++*	+++++*	+++++	+++++*
Acetone					
Isobutyraldehyde	+	+*	Trace	Trace	--
Butyraldehyde	+++	+++*	++	++	++
Butanone	+	+*	Trace	Trace	Trace
3-Methyl-2-butanone					
Diacetyl	+++++	+++++*	++++	++++	+++
Hexanal	Trace	Trace	Trace	Trace	Trace
2-Heptanone					
Heptaldehyde	+++++	+++++	++++	++++*	+++
Unknown	Trace	Trace	--	--	--
Unknown	Trace	Trace	--	--	--

\+ Represents the smallest relative peak height
* Slightly less than the number of +
Trace: Represents a slight hump

[a] From Ismail (1971)

TABLE 11

DATA ON COUNT, LENGTH AND CHEMICAL COMPOSITION OF DIFFERENT SPECIES OF PRAWNS[a]

(The values are averages of ten estimations)

	P. Caromatis	P. indicus	M. monoceros	M. brevicornis	P. sculptilis	P. maxillipedo	S. indicus	A. indicus
Counts/lb.	3-4	9-10	20-30	25-30	40-45	25-30	50-60	500-600
Length, cm.	22-30	15-17	10-12	12-15	9-12	12-15	7-10	1.5-2.5
Edible portion %	70.00	55.00	52.00	52.00	50.00	52.00	50.000	80.00
Moisture, %	67.50	70.10	77.20	78.10	79.20	68.30	80.100	79.90
Protein*, g/100 g	70.30	65.80	60.10	61.30	60.10	65.70	70.200	44.20
Fat*, g/100 g	5.10	4.90	4.50	4.80	3.50	4.60	3.100	1.50
Glycogen*, mg/100 g	315.00	318.000	318.000	213.000	218.000	223.000	415.000	435.000
Lactic acid*, mg/100 g	175.300	175.400	130.600	170.800	156.800	170.800	180.500	110.500
Vitamins, mg/100 g								
Ascorbic acid	Trace	4.100	5.000	3.200	2.800	2.600	Trace	4.800
Thiamine	0.015	0.016	0.009	0.013	0.011	0.013	0.008	0.014
Riboflavin	0.310	0.320	0.180	0.170	0.160	0.180	0.150	0.015
Niacin	4.600	4.500	4.300	3.900	3.800	4.600	3.900	2.100
Total Ash*, g/100 g	9.510	9.810	10.500	11.500	9.800	9.600	9.100	22.500
Minerals*, mg/100 g								
P	912.000	930.000	850.000	860.000	760.000	850.000	715.000	1975.000
Ca	470.000	510.000	535.000	525.000	515.000	510.000	495.000	825.000
Fe	27.600	32.700	37.300	36.400	42.600	43.100	37.200	50.500
Cu	22.500	29.700	40.300	33.000	36.100	34.800	38.100	45.800
Mo	0.100	0.100	0.200	0.200	0.300	0.200	0.300	0.400

* Calculated on dry-weight basis

[a] From Shaikhmahmud and Magar (1961)

TABLE 12

APPROXIMATE COMPOSITION[1] OF SHRIMP PROCESSED BY IRRADIATION AND OTHER METHODS[a]

Constituents	Fresh	Freeze Dried	Air Dried	Canned	Dehydro-shrimp	Dehydro-irradiated Shrimp		
						Air	Vacuum	Nitrogen
Moisture (%)	86.8	2.5	2.8	75.0	40.2	41.0	40.5	40.0
Protein	88.9	89.5	88.9	83.6	81.9	81.5	80.9	82.0
Nonprotein nitrogen	0.45	0.5	0.7	-----	0.4	0.5	0.45	0.5
Lipids	3.8	3.6	3.5	3.7	3.3	3.8	3.5	3.5
Ash	7.9	8.1	8.3	7.9	7.8	7.5	7.6	7.7
Ca	0.5	0.5	0.5	0.5	0.5	0.6	0.55	0.6
P	0.75	0.8	0.8	0.75	0.8	0.8	0.8	0.75

[1] Results, expressed on dry basis (% of total), are averages of triplicate analysis on three different batches of shrimp.

[a] From Srinivas et al. (1974)

TABLE 13

EFFECT OF GAMMA IRRADIATION ON THE SOLUBILITY OF SHRIMP PROTEINS[a]

Dose (kGy)	Grams of Protein Extracted/100 g Tissue			
	Water Soluble		5% salt soluble	
	Expt.1	Expt.2	Expt.1	Expt.2
0	2.25	3.31	6.25	7.88
1.0	2.31	3.31	6.00	7.18
2.0	2.19	3.34	5.63	7.00

[a] From Novak and Liuzzo (1964)

TABLE 14

TOTAL AMINO ACIDS IN SHRIMP PROCESSED

BY IRRADIATION AND OTHER METHODS[a]

Amino Acid	Fresh	Freeze-Dried	Air-Dried	Canned	Dehydro-shrimp	Dehydro-Irradiated Shrimp[1] Air	Vacuum	Nitrogen
	g per 16 g Nitrogen							
Aspartic Acid	11.02	11.00	10.90	11.08	11.05	11.02	11.08	11.05
Threonine	4.00	3.98	3.98	3.94	4.02	4.00	4.02	4.06
Serine	4.04	4.02	4.00	4.05	3.98	3.88	3.82	3.88
Glutamic Acid	20.12	20.45	21.60	20.80	20.14	21.25	20.02	21.06
Proline	2.18	2.24	2.09	2.19	2.28	2.26	2.28	2.30
Glycine	4.68	4.70	4.70	4.75	4.73	4.71	4.69	4.72
Alanine	6.04	6.01	6.05	6.02	6.02	5.88	5.86	5.79
½ Cystine	0.65	0.68	0.70	0.72	0.69	0.73	0.75	0.70
Valine	4.89	4.73	4.72	4.70	4.71	4.70	4.66	4.62
Methionine	2.80	2.81	2.58	2.65	2.79	2.74	2.78	2.76
Isoleucine	4.77	4.76	4.82	4.65	4.71	4.48	4.42	4.39
Leucine	8.55	8.53	8.32	8.38	8.23	7.97	7.88	7.85
Tyrosine	3.24	3.19	3.11	3.10	3.27	3.12	3.12	3.16
Phenylalanine	4.78	4.82	4.72	4.72	4.75	4.70	4.72	4.78
Lysine	8.28	8.23	7.62	7.67	8.23	8.39	8.41	8.44
Histidine	1.82	1.85	1.82	1.78	1.89	1.85	1.88	1.86
Arginine	7.29	7.20	7.08	7.11	8.42[2]	7.29	7.35	7.40
Tryptophan	1.56	1.58	1.45	1.40	1.56	1.54	1.56	1.55

[1] Irradiated at 2.5-3.2 kGy at ambient temperature.
[2] Probably an error.
[a] From Srinivas et al. (1974).

TABLE 15

EFFECTS OF GAMMA IRRADIATION AT -10°C ON THE AMINO ACID COMPOSITION OF GRASS SHRIMP[a]

Amino acid (weight percent)	Radiation Dose (kGy)				
	0.0	2.5	10.0	50.0	100.0
Lysine	9.1	8.9	8.7	8.8	8.9
Histidine	2.2	2.2	2.1	2.1	2.1
Arginine	9.3	9.0	9.7	9.3	9.1
Aspartic acid	10.4	10.3	9.9	10.0	10.1
Threonine	3.4	3.2	3.1	3.3	3.2
Serine	2.9	2.5	2.6	3.0	3.0
Glutamic acid	17.4	17.2	16.6	16.8	17.0
Proline	5.2	4.8	5.4	5.3	5.1
Glycine	6.8	6.7	7.2	7.0	6.6
Alanine	6.3	6.2	6.3	6.3	6.4
Valine	3.1	5.0	5.0	5.1	5.0
Methionine	2.8	2.2	2.5	2.3	2.6
Isoleucine	4.7	4.9	4.6	4.6	4.8
Leucine	8.3	8.2	7.9	8.0	8.3
Tyrosine	3.7	3.5	3.4	3.7	3.4
Phenylalanine	4.6	5.1	5.1	4.5	4.5

[a] From Yeh and Hau (1988)

TABLE 16

LIPID COMPOSITION OF INDIAN PRAWNS[a]

	Metapenaeus monoceros[1]	M. dobsoni	M. affinis	Penaeus indicus	Parapenaeopsis stylifera
Total lipid (g/100 g wet tissues)	0.7	1.2	1.0	1.0	1.0
Phospholipids (% of total lipids)	49	62	65	62	70
Triglycerides (% of total lipids)	9	11	14.5	14	10.5
Unsaponifiable matter (% of total lipids)	40.0	21.2	21.5	24.0	22.1
Cholesterol (% of unsaponifiable matter)	32	67	62	49	59

[1] Brackish-water species

[a] From Gopakumar and Nair (1975)

TABLE 17

FATTY ACIDS AS % WEIGHT OF TOTAL LIPIDS

IN PRAWNS[a]

Fatty Acids	Metapenaeus monoceros[1]	M. dobsoni	M. affinis	Penaeus indicus	Parapenaeopsis stylifera
Saturated					
12:0	-	-	0.5	-	-
13:0	-	0.4	0.2	0.2	0.5
14:0	3.0	1.9	3.8	2.5	1.5
15:0	1.7	0.7	1.2	0.6	1.0
16:0	32.5	24.3	20.6	26.3	22.3
17:0	2.4	2.2	2.7	0.9	1.4
18:0	9.8	13.1	14.2	12.1	11.7
Total	49.4	42.6	43.2	42.6	38.4
Monounsaturated					
14:1	-	-	-	1.8	-
15:1	-	0.8	-	-	0.9
16:1	6.7	9.3	8.6	8.0	8.1
17:1	Trace	0.9	1.8	0.4	1.2
18:1	12.1	11.2	15.2	11.5	13.1
20:1	0.5	0.7	1.0	0.9	0.7
22:1	0.8	-	-	0.1	-
24:1	-	-	0.6	-	-
Total	20.1	22.9	27.2	23.7	24.0
Polyunsaturated					
18:2	2.8	2.2	3.0	1.8	2.0
18:3	2.7	0.5	1.3	0.3	0.6
18:4	0.5	0.9	0.4	1.2	1.0
20:3	-	-	0.6	-	-
20:4	6.9	4.9	0.2	6.5	3.5
20:5	10.6	15.1	10.5	14.2	13.3
22:4	0.3	0.7	-	-	0.5
22:5	0.5	1.1	0.8	1.5	2.0
22:6	6.2	8.9	12.8	8.2	14.7
Total	30.5	34.3	29.6	33.7	37.6

[1] Brackish-water species

[a] From Gopakumar and Nair (1975)

TABLE 18

FATTY ACID COMPOSITION OF A FRESHWATER PRAWN (*Macrobrachium rasenbergii*) AND MARINE SHRIMP (*P. aztecus*)[a]

	Freshwater prawn			Marine shrimp		
Fatty Acid	TL[1]	PL[1]	TG[1]	TL[1]	PL[1]	TG[1]
16:0	26.0[2]	22.1[3]	28.7[4]	17.6[2]	23.7[3]	27.3[4]
16:1ω9	6.4	4.8	5.5	13.5	11.1	8.3
18:0	9.8	14.6	12.6	9.3	13.0	19.5
18:1ω9	28.8	25.0	24.2	14.9	13.8	13.5
18:2ω6	16.3	13.2	12.2	2.9	3.0	2.2
18:3ω6+20:1ω9	0.7	0.5	0.9	2.6	1.8	5.3
18:3ω3	1.9	1.5	1.4	1.5	1.3	-
20:2ω6	1.0	0.8	1.0	1.7	1.4	6.4
20:3ω6+22:1ω9	0.1	0.1	0.1	0.2	0.1	-
20:4ω6	2.7	5.2	1.1	6.4	5.5	1.2
20:5ω3	3.7	8.6	0.4	15.5	13.8	4.0
22:4ω6	0.2	-	3.0	0.8	0.8	-
22:5ω6	0.2	0.3	-	1.2	0.7	0.1
22:5ω3	0.2	0.2	1.8	1.5	1.2	9.9
22:6ω3	2.1	3.0	7.2	10.3	8.7	2.4
Total PUFA	28.3	32.8	28.1	41.8	36.4	26.2
Total ω6 PUFA	20.4	19.5	17.3	13.0	11.4	9.9
Total ω3 PUFA	7.9	13.3	10.8	28.8	25.0	16.3

[1] TL = Total Lipid; PL = Phospholipid; TG = Triglyceride
[2] Percent of total fatty acid
[3] Percent of phospholipid fatty acid
[4] Percent of triglyceride fatty acid

[a] From Chanmugan et al. (1983)

TABLE 19

FREE FATTY ACIDS IN IRRADIATED AND UNIRRADIATED SHRIMP[a]

Short-chain fatty acids[1]		
Compound (fatty acid)	Unirradiated Sample	Irradiated Sample (1.5 kGy)
C_1	0.0184	0.0086
C_2	0.0178	0.0189
C_3	0.8210	0.8431
C_4 (plus $isoC^4$)	1.315	1.3351
C_5 (plus $isoC^5$)	0.0072	0.0073
C_6	0.058	0.0745
Long chain fatty acids[2]		
C_{14}	0.0014	0.0016
C_{16}	0.0004	0.0004
C_{18}	0.0002	0.0002
C_{20}	0.0009	0.0004
C_{22}	0.0007	0.0008
$C_{22:1}$	0.0002	0.0001

[1] Expressed as moles in unspecified quantity of sample
[2] Expressed as peak area in square inches

[a] From Novak and Liuzzo (1964)

TABLE 20

RELATIVE ABUNDANCE[1] OF TOTAL FATTY ACID IN LIPID EXTRACTS FROM IRRADIATED AND UNIRRADIATED SHRIMP STORED IN ICE[a]

	0 kGy			1.5 kGy			8.0 kGy		
Fatty Acid	0 day	12 days	24 days	0 day	12 days	24 days	0 day	12 days	24 days
Myristic	0.42	0.73	0.88	0.68	0.42	0.89	0.94	1.31	1.29
Pentadecanoic	0.21	0.20	0.35	0.31	0.28	0.58	0.32	0.28	0.54
Palmitic	15.80	13.91	15.00	9.38	13.89	12.80	15.11	16.64	15.79
Heptadecanoic	--	--	--	--	--	--	--	--	--
Stearic	3.93	2.93	3.14	3.63	4.88	3.41	3.11	2.96	2.98
Myristoleic	Trace	Trace	<0.2	Trace	Trace	<0.2	Trace	Trace	<0.2
Palmitoleic	1.14	1.62	1.62	1.25	1.14	1.43	1.33	1.52	1.63
Heptadecanoleic	--	--	--	--	--	--	--	--	--
Oleic	9.10	7.42	7.56	9.44	10.68	9.05	10.44	10.83	11.09
Linoleic	Trace	Trace	Trace	0.56	0.79	0.98	1.00	1.04	0.98
Linolenic	0.29	0.34	0.31	0.36	0.31	0.34	0.34	0.52	0.58

[1] Arbitrary units

[a] From Ismail (1971)

TABLE 21

EFFECTS OF GAMMA IRRADIATION ON THE

FATTY ACID COMPOSITION OF GRASS SHRIMP[a]

Fatty acid (weight percent)	Dose (kGy)					
	0.0	2.5	5.0	10.0	50.0	100.0
$C_{16:0}$	38.3	37.6	36.9	38.3	37.4	39.3
$C_{18:0}$	19.1	16.9	19.8	18.1	19.6	18.4
$C_{18:1}$	26.5	28.7	26.2	27.0	25.9	27.7
$C_{18:2}$	16.1	16.8	17.2	16.6	17.2	14.7

[a] From Yeh and Hau (1988)

TABLE 22

CHOLESTEROL LEVEL IN IRRADIATED AND

UNIRRADIATED SHRIMP (mg/100 g DRY SHRIMP)[a]

Experiment	Irradiated[1]	Unirradiated
1	690	580
2	630	720
3	670	650
Mean ± S.D	663.3 ± 30.5	650.0 ± 70.0

[1] 10 kGy

[a] From Novak and Liuzzo (1964)

TABLE 23

B VITAMIN CONTENT OF PROCESSED AND DEHYDRO-IRRADIATED SHRIMP[a]

Vitamins	Fresh	Air dried (65 - 70°C)	Canned	Blanching and Partial Drying	Dehydro-Irradiated[b]		
					Air	Vacuum	Nitrogen
Thiamine (μg/100 g)	128.6	54.0 (58.0)[c]	50.2 (61.0)[c]	52.0 (59.0)[c]	33.5 (35.5)[d]	42.2 (18.9)[d]	40.6 (22.0)[d]
Riboflavin (μg/100 g)	250.0	144.5 (42.2)	144.5 (42.2)	122.5 (50.8)	104.4 (14.8)	112.4 (8.2)	110.0 (10.2)
Nicotinic acid (mg/100 g)	14.7	12.1 (15.0)	10.8 (26.8)	9.4 (36.6)	8.7 (8.0)	8.6 (8.4)	8.8 (6.9)
Vitamin B_{12} (μg/100 g)	18.4	12.3 (32.8)	11.2 (39.0)	11.4 (38.0)	10.4 (9.0)	10.4 (9.0)	10.1 (12.0)
Folic acid (μg/100 g)	57.1	33.9 (40.5)	31.9 (44.0)	29.3 (48.6)	23.9 (18.5)	25.9 (11.6)	25.5 (13.0)

[a] From Srinivas et al. (1974). Figures in parenthesis indicate percentage loss due to treatment.

[b] Dose = 2.5 - 3.2 kGy

[c] Compared with fresh shrimp.

[d] Compared with values for shrimp that was blanched and partially dehydrated.

TABLE 24

CHANGES IN SOME B VITAMINS[a] IN DEHYDRO-IRRADIATED SHRIMP ON STORAGE[1]

Vitamin	Semi-dried[2] (Storage period in days)		Irradiated semi-dried shrimp packed in								
			Air (Storage period in days)			Vacuum (Storage period in days)			Nitrogen (Storage period in days)		
	0[3]	30	0[3]	30	90	0[3]	30	90	0[3]	30	90
Thiamine	52.0	47.8	33.5	31.3	27.0	42.2	39.5	37.0	40.6	37.4	34.9
(μg/100 g)		(8.0)		(6.5)	(19.5)		(6.4)	(13.5)		(7.6)	(13.8)
Riboflavin	122.5	121.6	104.4	103.8	89.3	112.4	110.6	103.6	110.0	110.7	101.8
(μg/100 g)		(0.7)		(0.6)	(14.5)		(1.6)	(7.8)		(0)	(7.4)
Nicotinic acid	9.4	9.0	8.7	8.2	8.2	8.6	8.2	8.1	8.8	8.3	8.2
(mg/100 g)		(4.3)		(5.7)	(5.7)		(4.8)	(5.8)		(5.5)	(6.8)
Vitamin B_{12}	11.4	10.4	10.4	9.5	8.9	10.4	9.6	9.0	10.1	9.1	8.8
(μg/100 g)		(8.9)		(8.7)	(14.2)		(7.7)	(13.5)		(9.8)	(12.4)
Folic acid	29.3	26.6	23.9	21.8	19.1	25.9	23.7	21.8	25.5	23.5	21.0
(μg/100 g)		(9.3)		(8.8)	(19.9)		(8.4)	(15.8)		(7.7)	(17.6)

[1] Unirradiated and irradiated (2.5-3.2 kGy) semi-dried (40% moisture) shrimp samples were stored at 25-28°C. Values are on dry basis. Figures in parenthesis indicate percent loss over respective initial control values (0 day).

[2] Same as blanched partially dried shown in Table 23.

[3] From Table 23

[a] Data modified from Srinivas et al. (1974).

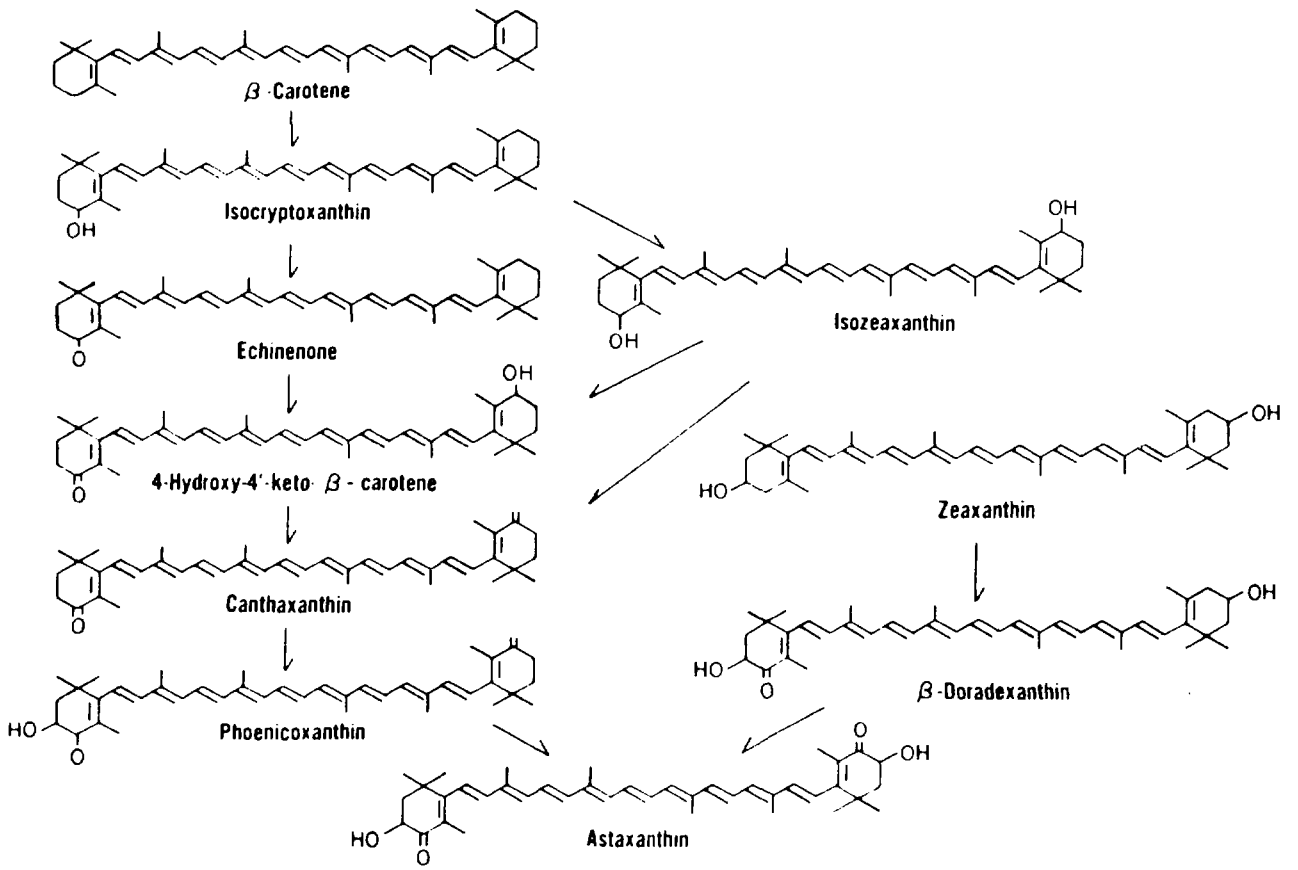

FIGURE 1: Postulated Conversions of Carotenoids for Prawn-Type Crustaceans From Simpson (1982)

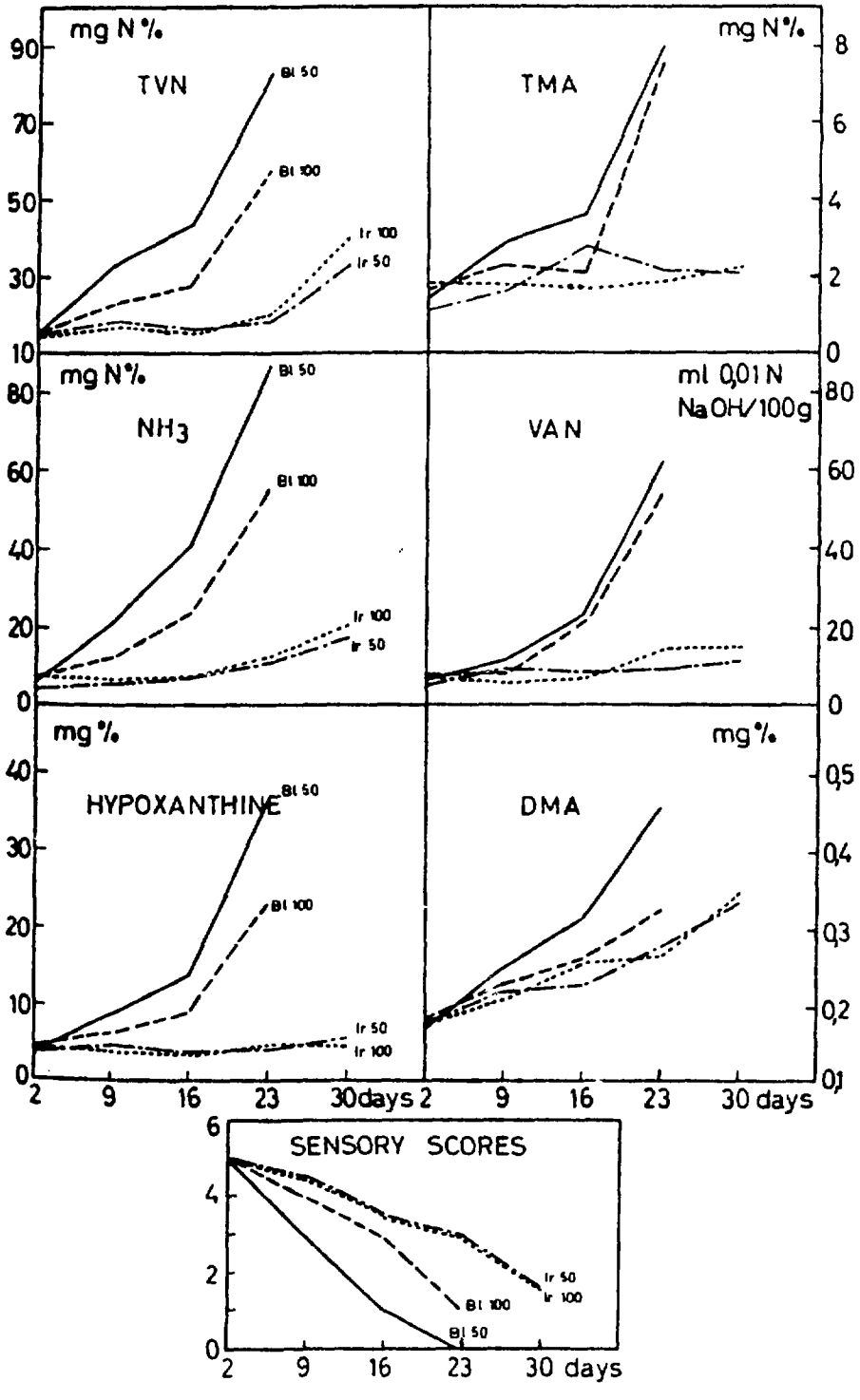

FIGURE 2: Chemical and Organoleptic Analyses of Irradiated (Ir) and Non-Irradiated (Bl) Peeled Shrimp Packed in 50- and 100-μm Pouches. TVN = Total volatile bases; VAN = total volatile acids; DMA = Dimethylamine; TMA = Trimethylamine. From Vyncke et al. (1976)

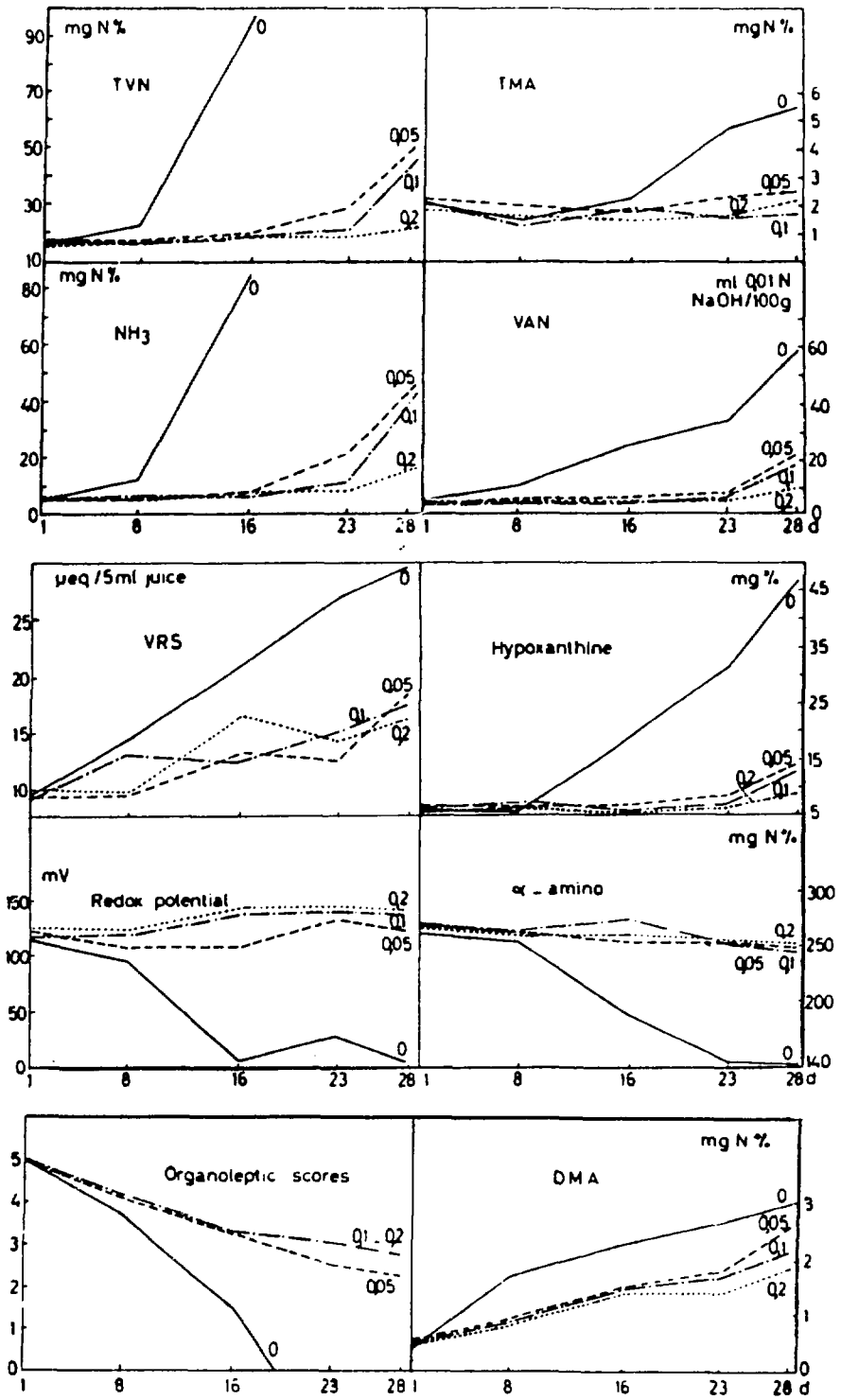

FIGURE 3: Chemical and Organoleptic Analyses of Irradiated Whole Shrimp. (0.5-1.0 and 2.0 kGy; control [0]). VRS = Volatile Reducing Substance; TVN = Total volatile bases; VAN = total volatile acids; DMA = Dimethylamine; TMA = Trimethylamine. From Vyncke and Declercke (1972)

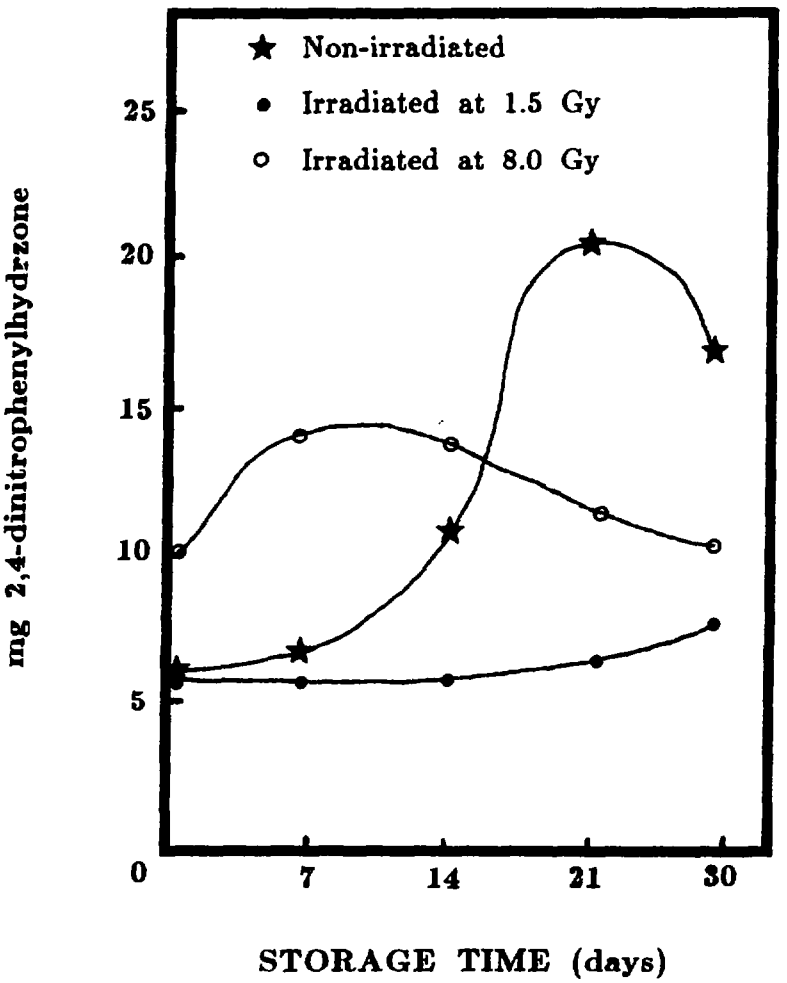

FIGURE 4: Effects of Irradiation on Total Carbonyl Compounds of Shrimp (measured as mg 2,4-dinitrophenylhydrazone per 100 g of shrimp) From Ismail (1971)

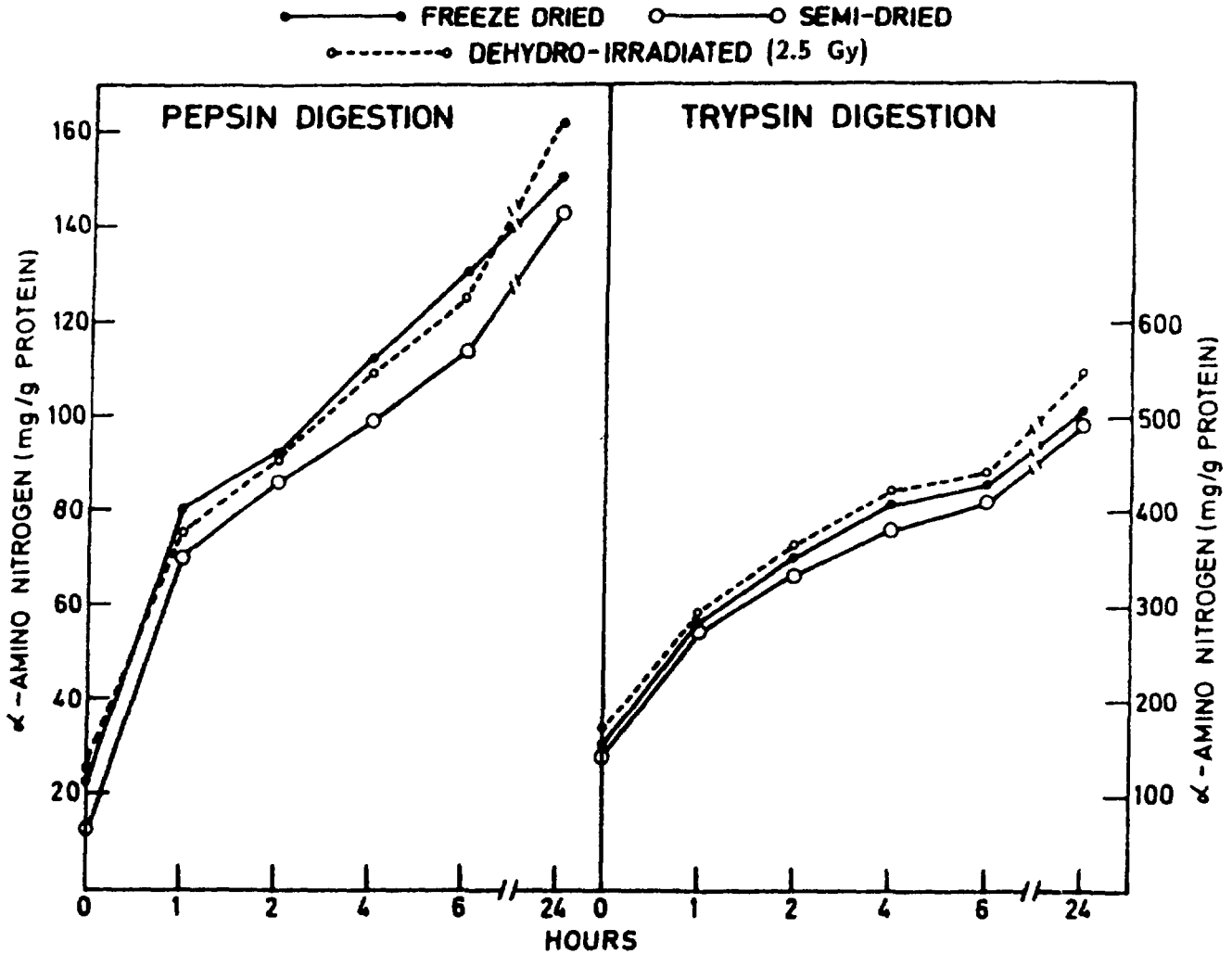

FIGURE 5: *In vitro* Digestibility of Processed Shrimp
From Srinivas et al. (1974)

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