

CHEMICAL QUALITY OF WHOLE, BEHEADED AND PEELED FROZEN SHRIMPS

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ABSTRACT

A total of 75 samples (25 of each) of imported frozen shrimps (whole, beheaded and peeled) were collected from different supermarkets in Alexandria governorate to evaluate their chemical quality. The results showed that peeled frozen shrimps had the highest mean values of acidity (PH) and total volatile nitrogen (T.V.N.) (6.5 ± 0.272 , 30.0 ± 0.218 ., respectively). Concerning total protein, indole contents, the whole and peeled frozen shrimps showed the highest levels (23.62 ± 1.348 ., 25 ± 0.676 ., respectively). Our results also indicated that peeled frozen shrimps had the highest mean concentrations of cholesterol (130 ± 1.832). In case of fatty acids composition., the whole frozen shrimp had a significant increase in Ecosenoic, palmitic and linoleic fatty acids with a mean values of 1724 ± 0.143 ., 18.543 ± 1.069 ., 10.729 ± 0.486 ., respectively. The highest mean concentrations of saturated fatty acids (41.802 ± 1.127) and total unsaturated fatty acids (61.485 ± 2.211) were in beheaded, whole frozen shrimps, respectively. At the same time, beheaded frozen shrimp showed the highest mean values of total n3 polyunsaturated fatty acids (5.773 ± 1.452 .) Regarding fat quality changes peeled frozen shrimps showed the highest mean concentrations of acid value., (2.342 ± 0.312 and free fatty acids (1.171 ± 0.235). In case of conjugated dienes and thiobarbituric acid reactive substances, beheaded frozen shrimp had the highest levels (0.04 ± 0.01 and 0.921 ± 0.092 ., respectively) At the mean time., the highest percent of total fat, was found in whole shrimp (1.58 ± 0.266). Concerning mineral composition, the whole frozen shrimp had the highest levels of manganese, copper, zinc, and calcium with a mean values of 1.225 p.p.m., 0.259 p.p.m., 0.129 p.p.m., 76.45 p.p.m., respectively. In case of iron, the highest level (39.0 p.p.m.) was found in beheaded shrimp. Regarding sodium and potassium, peeled shrimp had the highest mean concentrations of 200 p.p.m and 650 p.p.m., respectively. At the same time. cadmium, lead and mercury mean concentrations were within the standard permissible limits (0.1 p.p.m., 1.0 p.p.m., and 0.5 p.p.m., respectively), in all the examined shrimp samples. In case of boric acid, the whole frozen shrimp had the highest mean concentrations (66.435 ± 7.213).

INTRODUCTION

Shrimp has become a major port commodity and its production, processing and mar-

keting has become a major source of income of people in the industry. It is an excellent low calorie choice on the food chain. It is a rich

source of protein, vitamins and minerals (Kavun., 2008). Many varieties of shrimp are also low in sodium and cholesterol. It is also low in fat and most of the fat is polyunsaturated. Undeland., et al., 1999. Because many fats now specify polyunsaturated fat, rather than saturated fat, some frozen shrimp are relatively high in fat. However the fat is a primary unsaturated. It is also a good source of iron, phosphorus, potassium and zinc. Frozen shrimp are high in protein, low in sodium, and are rich in polyunsaturated fats, omega 3 fatty acids, which are believed to actively fight cholesterol build up and reduce the risk of heart disease. (Abdullah Oksuz., et al., 2009). Shell fish particularly, shrimp spoils more rapidly than fish for a number of reasons. Firstly, they are smaller, and small fish spoil more rapidly than larger ones. Secondly and more importantly, the gut is usually not removed immediately after capture, hence postmortem autolytic changes will occur faster. A third reason is that the chemical composition of shellfish tissue is different and it contains a lot of non-protein nitrogenous compounds that encourage more rapid spoilage (Shamshad., et al. 1990), Botta., (1995) and Zeng Qingzhu (2003). Since shrimp is important to human health due to its high nutritional value and it is one of the most perishable products and is susceptible to deterioration during storage and processing, therefore the purpose of this work is to evaluate the chemical quality of frozen shrimps .

MATERIALS AND METHODS

A total of 75 samples of frozen shrimp products, whole shrimp (shell on), beheaded shrimp and peeled shrimp ((25 for each) were selected randomly from Alexandria retail

stores. Samples were transferred in an insulated ice box to the laboratory and analyzed for chemical quality parameters.

- 1- **Hydrogen ion concentration (PH):** The pH of shrimp muscle was determined by using PH meter (Genway 3510 model) according to AOAC (1980).
- 2- **Total volatile basic nitrogen:** It was determined by steam distillation method using macrokjeldhal apparatus (Malle and Pourmeyrol 1998) .
- 3- **Total protein :** According to Pearson (1976) using macrokjeldhal apparatus .
- 4- **Indole :** It was estimated colourmetrically according to Carl ponder 1978.
- 5- **Cholesterol :** It was determined colourmetrically as described by Bohac., etal ..(1988).
- 6- **Fatty acids composition:** The methyl esters of extracted fish lipids were prepared according to Radwan, S. S., (1978) and fatty acids composition was determined by using Gas Liquid Chromatography (GLC) Shimadzu model according to Radwan., (1978).
- 7- **Acid number:** Acid number is defined as the number of milligrams of potassium hydroxide required to neutralize the free acid in 1 gm of the sample. It was determined According to Pearson 1976.
- 8- **Free fatty acids:** according to Pearson 1976
- 9- **Conjugated dienes:** It can be determined using ultraviolet (UV) -visible spectrophotometer .(Santlago., etal., 1997).
- 10- **Thiobarbituric acid reactive substances:** Fat was extracted using cold

extraction method and thiobarbituric acid reactive substances (TBARS) was determined colourimetrically according to Li., et al., 2001.

11- Total fat : using soxhelt apparatus for extraction of fat by petroleum ether (pearson., 1976).

12- Mineral composition (Mn, Cu, Fe, Zn, Na., Ca, K) : The principle of the minerals determination involved the production of acidic solution of the inorganic elements, after removing interfering materials by chelation solvent using ammonium pyrrolidine di-thio carbamate (APDC) and isobutyl methyl ketone (MIBK) After that minerals concentrations were determined by using flame atomic absorption spectrophotometer model perkin Elmer 2380 at wave length's specific to each element (Richard., 1986).

13- Contaminant levels (Cd, Pb, Hg): Cadmium and lead were determined by Hydrochloric-nitric (HCl-HNO₃) acid leaching method using flame atomic absorption spectrophotometer model Perkin Elmer 2380 (Richard, F., 1986). The principle of mercury (Hg) determination method depends on the conversion of all the Hg present in the sample into the inorganic form by wet oxidation and it's reduction to the metallic state. Then, the release of Hg from the solution as vapour using a stream of air followed by it's determination by flameless atomic absorption spectrophotometer (APHA/AWWA 1992).

14 - Boric acid: It was determined colourimetrically according to Shunjiro Ogawa., et al 1979.

RESULTS

Chemical quality of the examined frozen shrimps (whole, beheaded and peeled) are showed in Tables 1-7

DISCUSSION

Our results indicated that the highest level of acidity (pH) was found in peeled frozen shrimps (6.5) followed by beheaded (6.4) and whole frozen shrimps (6.2) with no significant difference between them. (Table1)

Zeng Qingzhu., 2003., mentioned that the initial pH of fresh shrimp was 7.41. Results show that the increases of pH value were rapid in samples that had been stored in ice at 1.5C^o and in salt- water ice at -1.5C^o, and reached 8.26 and 8.20, respectively. (Zeng Qingzhu., 2003).

The pH values less than 7.5 recorded by Shamshad., et al. (1990) even after the prawns were already spoiled especially at ambient storage could explain the problem using this parameter to evaluate the quality of shrimp (*Macrobrachium rosenbergii*.) Moreover, pH values should be combined with other indicators such as total volatile bases to be indicative of the shrimp quality. Lower pH values might have been caused by the production of lactic acid from glycogen degradation in the prawn meat, Shamshad., et al. (1990).

Middlebrooks et al., (1988), reported a maximum pH of 7.54 after only 4 hours of storage at ambient temperature, in farmed black tiger prawns., but thereafter the pH decreased to 7.2 and then tended to be relatively stable (Gelman et al., 1990).

Results from table (1) showed that, the highest level of total volatile nitrogen (30.0mg/100g) was in peeled frozen shrimps, while the lowest (28.5mg/100g) was found in whole, with no significant difference between them.

The total volatile nitrogen contents of whole shrimp samples stored at 4°C in a refrigerator were ranged from 22.95 mg/100g to 109.15 mg/100g. (Candan. et al. 2000).

The total volatile bases increased with time and temperature during storage. The initial levels of 17.0 mg/100g prawn sample increased continuously during frozen storage. A level of 30 mg/100g of muscle sample has been considered the upper limit above which fishery products are considered unfit for human consumption (Cheuk., et al. 1979 and Shamsbad., et al., 1990).

Iced storage shrimp samples showed that the upper limit of total volatile nitrogen (30 mg / 100 gm)was only reached between 12 to 16 days of storage. Based on chemical analysis. At 17th day of storage, the total volatile nitrogen contents were more than 30 mg/100g. (Farn and Sims., 1987).

It was found that the total volatile nitrogen of shrimp stored at zero degrees for one month showed the highest value of total volatile nitrogen (118.30mg /100g of sample)while the lowest was in fresh shrimp (30.96mg/100g) (Ibrahim., 2005).

The total volatile nitrogen of shrimp samples stored at -10 degrees for one month was 108.18mg/100kg (Canadian., et al. 2000).

Levels of TVBN in severely decomposed shrimp was > 60 mg/kg. (Rogério Mendes., et al., 2005), as well as a rapid increase in TVB at 10 degrees in shrimp(*Macrobrachium rosenbergii*) was detected due to the increase in total aerobic bacteria at elevated temperatures. (Abu Bakar., et al.; 2008), more over Amine. 2003 found that the total volatile nitrogen of frozen shrimp was 27.16 mg/100g. Also, the TVN for shrimp during cold storage was 39.8 mg/100gm (Christopher, Ellis and Mary LouSilva, 1997).

During automatic boiling, peeling and rinsing processes in shrimp factories, some of the water-soluble and volatile compounds will be extracted by the boiling water and possibly evaporated. In this investigation we have attempted to estimate the loss of TVN in shrimp muscle during this automatic processing. The results show that about 50% of the contents of TVN probably will be lost from the shrimps during automatic processing. Adding approximately 100% TVN to the analyzed contents in boiled, peeled and rinsed shrimps will therefore probably give the same level of these compounds as that found in the raw shrimps used (Solberg and Nesbakken., 1981).

Table (2) presented proximate composition of whole, beheaded and peeled frozen shrimps. It was found that the highest percent of protein was found in whole frozen shrimp (23.62%), while the lowest was in peeled shrimp (15.43%) respectively. There was a significant difference in percent of protein between the studied frozen shrimp samples at $p \leq 0.05$ (Table 2).

White shrimp meat (*Penaeus vannamei*)

had higher protein content than had black tiger shrimp meat (*Penaeus monodon*) (Pisal Sriket., et al., 2007).

The protein content was generally high in the shrimps. This higher protein content in shrimps is important from a dietary point of view since: the quality of fish protein is very high because of its essential amino acid composition. Fish muscle is more digestible than other animal protein due to lower level of connective tissue (Shamshad., et al 1990).

The proximate composition varies depending upon season, age, maturity, sex and availability of food (Karakoltsidis et al, 1995). During long starvation periods, fish and shellfish may utilize the protein in its body to survive. (Abdullah Oksuz et al., 2009).

Shrimps is considered as a high-range protein-containing nutrient like fish, which contain 8-20% protein; also its protein content was ranged between 17-21% depending on Shrimps species (Yanar and Celik, 2006 and Pisal Sriket., et al., 2007).

It was found that the protein content of crustaceans and mollusks were indicated around 20% (Silva and Chamul, 2000 and Abdullah Oksuz et al., 2009).

In the present study, the results of Table (3) indicated that the highest levels of indole was found in peeled shrimp (25microgm/100g) while the lowest was in whole frozen shrimp (20 microgm/100g) with a significant difference between them.

Indole detection has long been used as an

indicator of shrimp spoilage based on data collected by the food and drug administration (FDA) it defined a maximum allowable indole level of 25 microgm/100gm for canned pre-cooked frozen shrimps (Candan., et al., 2000).

Increased microbiological contamination induced faster and higher indole production at all temperatures. At higher storage temperatures, indole formation was greatly accelerated resulting in very high indole levels. High indole levels indicate decomposition; however decomposed shrimp may not necessarily contain indole.. (Fatima., et al, 1984, Candan., et al., 2000, Benner and Otwell., 2003, Snellings., et al 2003, Rogério Mendes., et al., 2005).

Shrimps (*Pandalus borealis*) caught in the Barents Sea and in shrimps caught outside Malaysia, India and Taiwan, stored in an ice and processed (boiled, peeled) showed that only low levels of indole had been formed during ice-storage. Not until an advanced state of spoilage could a distinct increase in the indole content in raw and in boiled, peeled shrimps be discerned.). most of samples of boiled, peeled shrimps from the Far East had high levels of indole which exceeded 25 microgram/100g. (Solberg and Nesbakken, 1981).

It was found that at low temperature storage(4 degrees), final indole levels in severely decomposed shrimp were much lower than the 25 g indole/100g shrimp . At higher storage temperatures, (12^o and 22^oC), indole formation was greatly accelerated resulting in very high indole levels.. Frozen storage and

cooking had little effect on indole levels. (Olivia chang, I et al., 1983).

The data presented in Table (4) revealed that highest mean concentrations of cholesterol was 130mg/100g.

The overall average of cholesterol for several species of shrimp from several different geographical locations was 152 ± 15 mg/100g of edible portion of shrimp. Samples of *Pandalus borealis*, Gloucester prawns and Canadian prawns, accounted for the low (136 mg/100g) and the high (186 mg/100g) limits, respectively, of the range of cholesterol. (Judith., et al., 2006).

Reported values of the cholesterol content in shrimp vary considerably. The possible factors causing this variation were method of analysis, season, diet, size, ovarian development, and species. Species and seasonal differences caused significant variation in the cholesterol content. The reported values of cholesterol in shrimp were ranged from 125 to 200 mg/100 g, (Kritchevsky and Tepper 1961, Feeley et al 1972, Thompson, 1964 and Kritchevsky et al., (1967).

Results of Table (4) illustrated the fat changes in frozen shrimps (whole, beheaded and peeled). Results of lipid hydrolysis showed that the highest mean values of acid number and free fatty acids (2.342mgKOH/g of fat, 1.171ml/g) were in peeled shrimp., respectively., while the lowest were in whole (4.480mg/gm, 2.24 0ml/gm) with a high significant difference between them. Concerning, lipid oxidation changes (CD, TBA), beheaded had the highest value (0.04nmole/mg,

0.921mg/kg), while the lowest was in whole (0.01n mole/mg,0.789mg/kg) with no significant difference in the levels of CD and TBARS between the examined samples, more over, Ibrahim., (2006) reported that fresh shrimp showed the lowest free fatty acids levels (1.03 ml/gm) while the highest (4.467ml/gm) was in shrimp stored at -10 c for 10 months .Concerning acid value, fresh shrimp had the lowest value (2.06mg KOH/gm of fat), while shrimp stored for one month at -10 c showed the highest (5.262mg KOH/gm of fat). Regarding lipid oxidation parameters (CD, TBA) the conjugated dienes decreased with the progress of spoilage during storage at different temperatures (at zero degree in ice, 4 degrees in refrigerator and at -10 degrees in freezer) and the vice versa was true for TBA values. The highest levels of CD and TBARS (0.054nmole/mg 3.980mg malonaldehyde/kg) were found in shrimp stored in ice at zero and in shrimp stored at -10 degrees for one month, also, TBA act as an index for lipid oxidation revealed highly significant changes in farm, marine and frozen shrimps with the highest mean value of 0.801 in frozen shrimp then 0.308 and 0.182 in farm, marine shrimp., respectively (Amine., 2003). while T.B.A. in food value above 1-2 mg/kgm fat will probably have rancid flavours, (Connell., et al., 1975).

Table (5) showed Fatty acids composition of frozen shrimps (whole, beheaded and peeled) (n=25). Gas liquid chromatography identified 28 fatty acids in variable concentrations in whole and beheaded and peeled frozen shrimps. The mean values of total saturated fatty acids were (38.631%, 41.802%, 39.747%) in whole, beheaded and peeled

frozen shrimps, respectively. At the same time, the total unsaturated fatty acids showed mean values of 61.485%, 58.198%, and 57.492% in whole, beheaded and peeled frozen shrimps, respectively. The highest significant percent of Palmitic (C16:0) (the key of fish metabolism (18.543%), was found in whole frozen shrimp and the lowest (16.402%), was in peeled frozen shrimps, while the highest significant percent of EPA (C20:5) n-3, (C22:5) n-3, were in whole frozen shrimps with mean values of 1.003%, 1.124%, respectively, while the highest percent of DHA (C22:6) n3 was in beheaded frozen shrimp (4.316%). The increase in saturated fatty acids in may be attributed to the transformation (saturation) of some of the monounsaturated fatty acids and or polyunsaturated. Saturated fatty acids results from direct feeding on the phytoplankton and or feeding on fish that had already fed on phytoplankton (Gopakumar and Nair 1972).

Fatty acids profile of *P. longirostris* and *P. martia* showed that Palmitic acid was the dominant fatty acid in total saturated fatty acids in both species. The amount of palmitic acid of *P. longirostris* (20.27%) was almost the same as *P. martia* (20.14%) ($p > 0.01$) (Abdullah Oksuz et al., 2009), also they reported that black tiger Shrimps showed palmitic acid's mean concentration of 22.2% and white tiger Shrimps had a level of 21.8% (Sriket et al., 2007). In addition, DHA and EPA, belonging to n-3 fatty acids family, are considered as essential (Fellz et al., 2002). DHA and EPA, two of the major PUFA were found as 18.98 and 13.84% in the *P. longirostris*' of total fatty acids and 15.59 and 12.84 in *P. martia*'s of total fatty acids, respectively (Abdullah

Oksuz et al., 2009), on the other hand, polyunsaturated fatty acids were found as the major fatty acids in shrimp. With the range of 42.2-44.4%. DHA (22:6)/EPA (20:5) ratio in black tiger shrimp (2.15) was higher than that in white shrimp (1.05). Pisal Sriket., et al., (2007).

All shrimps (black tiger shrimp and white shrimp) were low in fat at about 1%. Elcospentaenoic and docosahexaenoic acids were present at about 30% of the total fatty acids, providing about 0.20g/100g in the edible portion. Judith., et al., (2006).

Ackman (1989), reported that the shellfish tend to have EPA greater than DHA.

Lipid contains mostly polyunsaturated fatty acids (essential fatty acids), which includes linoleic acid and alpha-linolenic acid that are parent compounds of Omega-6 and Omega-3 fatty acid series, respectively. These essential fatty acids are available in shrimp provides health benefits for humans e.g., eye (retina) and brain development and functioning, nutrient for growth and development of human body (Simopolous, 1991, Conner, 1992, Anon, 1994, Osborn and Akoh., 2002, Abdullah Oksuz., et al., 2009).

Table (2) presented proximate composition of whole, beheaded and peeled frozen shrimps. Results showed that the highest percent of fat was found in whole frozen shrimp (1.58%.) while the lowest was in beheaded shrimp (0.23%.) respectively. There was a significant difference in percent of fat between the studied frozen shrimp samples at $p < 0.05$.

The lipid content in three marine shrimp species in the Venezuelan internal market, two of them are native species, from fisheries, *Farfantapenaeus brasiliensis* and *Litopenaeus schmitti*, and one is an exotic species and farmed, *L. vannamei*, under different culture conditions (e.g. feed used), are ranged from 4.8 to 10.9%. At the same time, there were detected differences between the lipid content and fatty acids composition of the species. Wild *L. schmitti* had the highest lipid content (10.9%), following by wild *F. brasiliensis* (9.0%), cultured *L. schmitti* (4.8% to 7.1%) and cultured *L. vannamei* (5.1% to 6.2%). (Cabrera, et al., 2005).

Crude lipid levels was found as 1.55% in muscle of *P. longirostris* and as 1.01 % in that of *P. martia* (Abdullah Oksuz., et al., 2009).

Our results revealed that the whole frozen shrimp had the highest levels of manganese (Mn), copper (Cu), iron (Fe), zinc (Zn), and calcium (Ca) with mean values of 1.225 p.p.m., 0.259 p.p.m., 23.30 p.p.m., 0.129, 76.45 p.p.m., respectively., concerning, iron the mean concentration was found in beheaded frozen shrimp (39p.p.m.), while in case of sodium (Na) and potassium (K), peeled shrimp had the highest mean concentrations (200p.p.m., 650p.p.m., respectively). At the same time, cadmium, lead and mercury mean concentrations were within the standard permissible limits (0.1p.p.m., 1.0 p.p.m., and 0.5p.p.m., respectively) (Table 6).

Concentration levels of toxic heavy metals such as Cd, Hg, As, Pb, Cu, and Zn in edible tissues of fish and shrimp species collected from Manifa and Tarut regions in Gulf of Sau-

di Arabian were found to lie well within the Saudi Arabian Standards Organization limits. (Saad Al-Sulami, et al, 2002).

Ibrahim., 2001 reported that the mean values of cadmium, lead and mercury in shrimp collected from Elmex Bay in Alexandria were 0.359 p.p.m., 0.974 p.p.m. and 0.024p.p.m., respectively while shrimp collected from Abukir area showed cadmium, lead and mercury levels of 0.130, 1.248, 0.622., respectively. Shrimp from Maruit area (fish farm) Cd, Pb, Hg were 0.149 p.p.m., 1.055 p.p.m., 0.008., respectively.

Heavy metals are considered the most important form of pollution of the aquatic environment because of their toxicity and accumulation by marine organisms like shrimp (Khansari et al, 2005). Heavy metals are classified as: Potentially toxic (e.g., aluminum, arsenic, cadmium, lead, mercury, cadmium), probably essential (e.g., nickel, vanadium, cobalt) and essential (e.g., copper, zinc, selenium) (Olivas and Cámara, 2001). Some heavy metals, such as arsenic, lead and cadmium, are toxic and even a small amount of availability of these metals in shrimp can be very harmful to human health (Khansari et al, 2005).

Reports on the chemical composition and functional properties of prawns in Nigeria indicate that prawns contain a good amount of sodium. (Schamschula, et al., 1988 and Beauchamp, Engelman, 1991).

Shell fish are relatively good sources of macrominerals, including calcium, phosphorus, magnesium and potassium. (Erkanand

Ozden, 2007). The ratio of sodium to potassium ranged from 1:4 to 1:15. they are excellent sources of the trace elements, including copper, iron, zinc and manganese. (Lovell, 1989 Anon, 2004, and Whithney and Rolfes, 2008 , Abdullah Oksuz et al., 2009).

Gokoglu, et al., 2008, reported that high levels of Copper (Cu) (6.19 mg kg^{-1}), cadmium (Cd) (2.36 mg kg^{-1}), zinc (Zn) (30.84 mg kg^{-1}) and iron (Fe) (33.89 mg kg^{-1}), were found in edible tissue of *P. semisulcatus* and the highest Mn (1.52 mg kg^{-1}) concentrations were found in shrimp (*P. longirostris*) from the Gulf of Antalya, Turkey while the lowest Cu (1.33 mg kg^{-1}), Cd (0.23 mg kg^{-1}), Zn (6.25 mg kg^{-1}), Fe (1.84 mg kg^{-1}) and Mn (0.25 mg kg^{-1}) concentrations were in *P. serratu*. At the same time., there were significant differences in trace element concentrations among shrimp species, while Abdullah Oksuz et al., 2009 found that the highest mean values of macroelements (K, P, Na and Ca) of *P. longirostris* were 996 mg kg^{-1} , 993 mg kg^{-1} , 876 mg kg^{-1} , and 495 mg kg^{-1} , respectively., while those of *P. martia* were 1344 mg kg^{-1} , $644.96 \text{ mg kg}^{-1}$, 578.8 mg kg^{-1} , and 574.8 mg kg^{-1} , respectively. (Abdullah Oksuz et al., 2009). The highest concentrations of macroelements (iron, zinc and copper) in *P. longirostris* were 18, 6.1 and 2.2 mg kg^{-1} respectively. In addition, very small amount of Cd, Mn and Cr were also detected in *P. longirostris* with values of 0.784 mg kg^{-1} , 0.729 mg kg^{-1} , and 0.098 mg kg^{-1} , correspondingly. On the other hand, similar results were observed for *P. martia*.

Iron is one of the very important essential trace elements since it has several vital func-

tions in human system. It serves as a carrier of oxygen to tissues from the lungs by red blood cell. Adequate Fe in diet is very important for avoiding some major health problems (Belitz and Grosch, 2001; Cámara et al., 2005, Kavun., 2008). However, according to Institute of Turkish Standard (ITS, 2000), exceeding level of 10 mg kg^{-1} for iron is not permitted. green tiger shrimp, speckled shrimp and *Aristeus antennatus* had iron mean concentrations of $1.48 \text{ mg}/100 \text{ g}$, $1.55 \text{ mg}/100 \text{ g}$ and $0.9 \text{ mg}/100 \text{ g}$ respectively. (Karakolsidis et al., 1995 and Yanar and Celik, 2006).

High amounts of copper are present in crustaceans, decapods, gastropods and cephalopods that use copper in their haemocyanins to carry oxygen to their tissues. Despite the high copper concentrations in some molluscan and crustacean shellfish, copper concentrations in aquatic food present no problem for human health (White and Rainbow, 1985 and Oehlenschläger, 2002). Copper has been known one of the major catalysts for oxidation (Thanonkaew et al., 2006). It was found that Cu, Cd and Zn were found as 2.2, 0.7 and 6.1 mg kg^{-1} for *P. longirostris* and 2.8, 0.14 and 5.8 for *P. martia*, respectively. Except Zinc and Chromium, all the elements were significantly different in both shrimp species. According to ITS (2000), tolerance level of Cu, Cd and Zn in food should not exceed 5, 0.1 and 50 mg kg^{-1} ($500 \text{ mg}/100 \text{ g}$), respectively. The levels of Zn in *P. longirostris* and *P. martia* was not exceed the limit. Additionally, Gokoglu et al. (2008) reported levels of Cu, Cd and Zn for *P. longirostris* as 1.33, 0.23 and 14, 57 mg kg^{-1} . Anon, 2004, Gokoglu et al., 2008 and Abdullah Oksuz et al., 2009).

It is pointed out that the main functions of essential minerals are regulation of acid- base equilibrium. Minerals also constitute important components of enzymes, hormones and enzyme activators (Belitz and Grosch, 2001).

It was reported that the highest boric acid level was in frozen whole shrimp (66.435p.p.m.) while the lowest was in peeled shrimp (48.698p.p.m.) (Table 7).

Boric acid is not allowed as a food additive. However because of its antiseptic effect, it is sometimes used illegally to preserve imported sea food such as frozen shrimp and prawns. Borate in imported shrimp should not exceed-

ed 150 p.p.m.. Levels of boric acid (p.p.m) in frozen shrimp with shells were 67.9p.p.m. at the same time peeled frozen shrimp had boric acid mean concentration of 60 p.p.m. . (Shunjiro Ogawa..etal 1979).

CONCLUSION

We can conclude that:

- 1- From results of this study, it was indicated that the imported frozen shrimp samples were of good chemical quality.
- 2- It is recommended to evaluate the microbial quality of imported frozen shrimps.

Table (1) : Mean values of hydrogen ion concentration (pH) and total volatile nitrogen content (T.V.N.) of frozen shrimps (whole, beheaded and peeled).

Frozen shrimps	Hydrogen ion conc.(PH)	Total volatile nitrogen (T.V.N.) (mg/100gm)
	Mean± S.D	Mean ±S.D
Whole (shell on)	6.2 ±0.132	28.5±0.145
Beheaded (shell on, head off)	6.4 ±0.131	29.0±0.268
Peeled (shell off)	6.5 ±0.272	30.0±0.218

Table (2) : Mean values of proximate composition (Total proteins % and Total lipids %) of frozen shrimps(whole,beheaded and peeled) .

Frozen shrimps	Total proteins (%)	Total lipids (%)
	Mean±S.D	Mean±S.D
W hole frozen	23.62±1.348*	1.58± 0.266*
Beheaded	18.70±1.760 *	0.23±0.194*
Peeled	15.43±1.942*	0.24±0.148*

* Significant at P≤ 0.05

Table (3): Mean values of indole levels of frozen shrimps(whole, beheaded and peeled).

Frozen shrimps	Indole levels (Mean± S.D)
Frozen whole	20±0.643*
Beheaded	23±0.436*
Peeled	25±0.676*

* Significant at P≤ 0.05

Table (4): Mean values of fat quality indicators of frozen shrimps (whole,beheaded and peeled).

Frozen shrimps	Cholesterol (mg/100 gm)	Acid number [mg KOH/g of fat]	Free fatty acids (ml/gm)	Conjugated dienes (n mole/mg)	TBARS [mg malonaldehyde / kg of sample]
whole	125± 2.054 *	2.480± 0.293*	1.240± 0.145	0.01±0.008	0.789± 0.054
Beheaded	128± 1.636 *	2.860± 0.353*	1.430± 0.191	0.04± 0.01	0.921±0.092
Peeled	130± 1.832 *	2.342± 0.312*	1.171± 0.235	0.02± 0.009	0.864± 0.064

* Significant at P≤ 0.05

Table (5): Mean values of fatty acids composition of frozen shrimps (whole, beheaded and peeled).

Fatty acids	Whole	Beheaded	Peeled
C6	1.305±0.185*	1.086±0.165*	1.850±0.168*
C8	0.059±0.016*	1.044±0.312*	1.078±0.428*
C10	0.239±0.189*	1.311±0.415*	1.559±0.0.542*
C12	0.702±0.231*	1.270±0.510*	2.030±0.493*
C13	0.228±0.165*	1.374±0.562*	1.845±0.601*
Myristic(C _{14:0})	3.544±0.196	3.219±0.923	3.306±0.816
C14:1	0.118±0.046*	1.060±0.123*	1.119±0.346*
pentadecanoic (C _{15:0})	0.306±0.102*	1.141±0.131*	1.129±0.161*
C15:1	0.069±0.010	1.075±0.298	1.110±0.184
Palmitic (C _{16:0})	18.543±1.069*	17.835±1.164*	16.402±1.049*
Palmitoleic (C _{16:1})	4.149±0.913*	4.516±0.385*	2.405±0.569*
heptadecanoic (C _{17:0})	0.541±0.176	0.332±0.169	1.256±0.631
C17:1	0.123±0.081	0.091±0.021	1.071±0.641
Stearic (C _{18:0})	4.933±0.536	4.287±0.136	4.225±0.265
Oleic (C _{18:1})	28.735±0.675*	27.525±0.917*	29.234±0.821*
Lenoleic (C _{18:2})	10.729±0.486*	8.171±0.614*	6.634±0.148 *
Lenolenic (C _{18:3})	1.623±0.375	0.508±0.167	1.415±0.167
Arachidic (C _{20:0})	6.114±1.152	5.047±0.345	5.067±0.218
Eicosenoic (C _{20:1})	1.724±0.143	0.903±0.213	1.636±0.148
C20:2	0.124±0.073	0.421±0.115	1.214±0.121
C20:3	0.104±0.021	1.563±0.165	1.376±0.179
C20:4	2.565±0.838	1.365±0.167	0.481±0.287
EPA (C _{20:5}) n-3	1.003±0.103	0.923±0.258	0.632±0.216
C22:1	6.143±1.585*	5.094±0.521*	4.049±0.189*
C22:2	0.180±0.048	0.133±0.021	0.059±0.023
(C _{22:3}) n-3	1.124±0.455	0.810±0.167	0.741±0.198
DHA (C _{22:6}) n-3	2.856±0.846 *	4.040±0.651*	4.316±0.238
C24:0	2.1166±0.972*	3.856±0.512*	2.761±0.231
total Saturated fatty acids	38.631±1.123*	41.802±1.127*	39.747±1.214*
total Unsaturated fatty acids	61.485±2.211*	58.198±2.121*	57.492±2.165*
total n3 polyunsaturated fatty acids	4.983±1.832*	5.773±1.452*	5.689±1.518*

* Significant at P<0.05

Table (6) : Mean concentrations of trace elements (p.p.m) in frozen shrimps (whole,beheaded and peeled).

Frozen shrimps	Trace elements (mean concentrations)									
	Mn	Cu	Fe	Zn	Na	Ca	K	Cd	Pb	Hg
Whole	1.225	0.259	23.30*	0.129	145*	76.45*	550*	0.017	0.225	0.05
Beheaded	0.414	0.243	39.00*	0.061	185*	41.55*	600*	0.007	0.120	0.04
Behpeeled	0.129	0.196	35.50*	0.055	200*	34.60*	650*	0.040	0.100	0.08

* Significant at P≤ 0.05.

Table (7) : Mean concentrations of boric acid in frozen shrimps(whole, beheaded and peeled) .

Boric acid (Mean± SD)	Frozen shrimps
66.435± 7.213*	Frozen whole
59.432± 6.768*	Beheaded shrimp
48.698± 4.943*	Peeled

* Significant at P≤ 0.05.

REFERENCES

- Kritchevsky, D. and Tepper, S. A. (1961)** : The free and ester sterol content of various foodstuffs. *J. Nutrition*. 74: 441.
- Thompson, M. H. (1964)** : Cholesterol content of various species of shellfish. I. Method of analysis and preliminary survey of variables. *Fishery Ind. Research* 2(3): 11
- Kritchevsky, D.; Tepper, S. A.; DiTullo, N. W. and Holmes, W. L. (1967)** : The sterols of seafood. *J. Food Science*. 32: 64.
- Feeley, R. M.; Criner, P. E. and Watt, B. K. (1972)** : Cholesterol content of foods. *J. American Dietetic Association*. 61(2): 134.
- Connell, J. J. (1975)** : Control of fish quality. Fishing News (Books) Ltd., Farnham, Surrey, UK.
- Pearson, D. (1976)** : Laboratory techniques in food analysis, London, Boston, Butterworth, Co.Ltd.1976.51-75.
- Carl ponder (1978)** : Decomposition in Foods (chemical methods).Fluorometric determination of indole in shrimp. *J. AOAC*, 61 (5):1089-1091.
- Radwan S. S., (1978)** : Copling of two dimension thin layer chromatography with gas chromatography for quantitative analysis of lipid classes constituent fatty acids , *journal of chromatographic science*, 16:538.
- Cheuk, W. L.; Finne, G. and Nickelson, R. (1979)** : Stability of adenosine deaminase and adenosine monophosphate deaminase during storage of pink and brown shrimp from the Gulf of Mexico.*J.Food.sci.*44:1625-1630.
- Association of official analytical chemists (A.O.A.C.) (1960)** : Official methods of analysis, 13th ed . AOAC,Arlinoblon,V.A. N
- Solberg T. and Nesbakken T. (1981)** : [Quality changes in iced shrimps (*Pandalus borealis*). III. Indole and pH in shrimps caught in the Barents Sea compared with shrimps caught in the Far East (author's transl). *Nord Vet Med.* 1981: 33(4-5):250-9 (ISSN: 0029-1579).
- Olivia Chang, Wailun Cheuk, Ranzell N., Roymatin and Gunnar, F. (1983)** : Indole in Shrimp: Effect of Fresh Storage Temperature. Freezing and Boiling.*Journal of Food Science* Volume 48 Issue 3, Pages 813 - 816.
- White, S. L. and Rainbow, P. S.. (1965)** : On the metabolic requirements for copper and zinc in molluscs and Crustaceans. *Mar. Environ. Res.*, 16: 215-229.
- Middlebrooks, B. L.; Toom, P. M.; Douglas, W. L.; Harrison, R. E. and McDowell, S. (1988)** : Effect of storage time and temperature on the microflora and amine development in spanish mackerel (*Scomberomus maculatus*). *Journal of Food Science*. 53 : 1024-1029.
- Fatima, R.; Khan, M. A. and Gadri, R. B. (1988)** : Shelf life of shrimp (*Penaeus mergulensis*) stored in ice (0°C) and partially frozen (-3°C). *J. Sci. Food Agric.* 42. 235-247.

Bohac., C. E.; Rhee, K. S.; Cross, H. R. and Kon, O. (1988) : Assessment of methodologies for colorimetric cholesterol assay of meats. *J. Food. Sci.* 53:1642-1644.

Lovell., T. (1989) : Nutrition and feeding of fish. New York. Van nostrand reinhold, pp: 260.

Ackman, R. G. (1989) : Nutritional composition of fats in seafood in progress. *Food Nutr. Sci.*, 13: 161-241.

Gelman, Pasteur, R. and Rave, M. (1990) : Quality changes and storage life of common carp (*Cyprinus carpio*) at various storage temperatures. *Journal of the Science, Food and Agriculture.* 52: 231-247.

Shamshad, S. I.; Kher Un, N.; Riaz, M.; Zuberi, R. and Qadri, R. B. (1990) : Shelf life of shrimp (*Penaeus merguensis*) stored at different temperatures. *J. Food Sci.* 55(5):1201-1205.

Imopolous, A. P. (1991) : Omega-3 fatty acids in health and disease and development. *Am. J. Clinical Nutr.*, 54: 438-63.

APHA/AWWA (1992) : Standard methods for examination of water and wastewater, 18th ed. Joint of APHA/AWWA, Washington DC.

Conner, W. E.; Neuringer, M. and Reistick, S. (1992) : Essential fatty acids: The importance of n-3 fatty acids in the retina and brain. *Nutr. Rev.*, 50: 21-9.

Egyptian organization for standardiza-

tion and quality control (1993) : Maximum levels for heavy metals contamination in food E.S.No. 2360 .

AOAC (1995) : Official methods of analysis, 16 ed. Association of official analytical chemist, washington.DC.

Botta J. R. (1995) : Evaluation of sea food freshness quality .VCH Publishers Inc .

Karakoltsidis, P. A.; Zotos A. and Constantinides M. (1995) : Composition of the commercially important Mediterranean fin-fish, crustaceans and mollusks. *J. Food Composition Anal.*, 8: 258-273.

Christopher, P.; Ellis. and Mary LouSilva (1997) : Statistical classification of sea food quality .*Journal of AOAC.* Int.80(6):1347-1353.

Malle and Poumeryrol (1998) : Anew chemical Criterion for the quality control of fish : TMA/TVBN(%). *J. Food. Prot.* 52 (6) : 419-423.

Undeland. I. and Hans Lingnert (1999) : Lipid oxidation in Fillets of herring (*Clupea harengus*) during frozen storage. Influence of prefreezing storage. *J. Agri. Food. Chem.* 47:2075-2081.

Candan, V.; Tacnur, B.; Ozhan. O. and Mentin, S. (2000) : Sensory evaluation and determination of some physical and chemical characteristics of shrimp during cold storage . *Turk.J.Vet.Animal.Sci.*,24:181-186.

ITS, (2000) : The Ministry of the Agricul-

ture of Turkey. Rep. 5.

Beltz, H. D. and Grosch W. (2001) : Schieberle, P. Lehrbuch der Lebensmittelchemie, ISBN: 3-540-41096-15. Springer Verlag, Berlin Heidelberg New York.

Li, C. T.; Wick, M. and Marriott, N. G. (2001) : Evaluation of lipid oxidation in animal fat. Bull Ohio state University, research and Reviews: Meat Special circular 172: 99-104.

Ibrahim, M. K. (2001) : The effect of water pollution on hygienic condition of fish. Thesis of PhD in public health sciences .. High Institute of public health, Alexandria university, 2001.

Olivas, R. and Cámara, C. (2001) : Speciation Related to Human Health. In: Epton, L., L. Pitts, R. Cornells, H. Crews, O.F.X. Donarand P. Quevauviller (Eds.). Trace Element Speciation for Environment Food and Health. The Royal Society of Chemistry.

Osborn, H. T. and Akoh, C. C. (2002) : Structured lipids- Novel fats with Medical, and Food applications. Comprehensive Reviews in Food Science and Food Safety, Institute of Food Technologists. : 93-103.

Oehlenschläger, J. (2002) : Identifying Heavy Metals in Fish, Chapter 7. Safety and Quality Issues in Fish Processing. In: Allan Bremner, H. (Ed.), CRS press, Woodhead Publishing Limited, Cambridge, England. Wiley-VCH.

Saad Al-Sulami, Ahmed M. Al-Hassan,

Mohammad Dall and Kither N. M. (2002) : Study on the distribution of toxic heavy metals in the fishes, sediments & waters of Arabian Gulf along the eastern coast of Saudi Arabia. Technical Report No. APP 3803/96011, October 2002.

Fellz, G. L. A.; Gatlin, M. D.; Lawrence L. A. and Valezquez, P. M. (2002) : Effect of dietary phospholipid on essential fatty acid requirements and tissue lipid composition of *Litopenaeus vannamei* juveniles. *Aquae*, 207 : 151-167.

Zeng Qingshu (2003) : Quality Indicators of Northern (*Pandalus borealis*) Stored under Different Cooling Conditions. UNU-Fisheries Training Programme., ICELAND.

Benner, R. A. and Otwell, W. S. (2003) : Evaluation of putrescine, cadaverine and indole as a chemical indicator of decomposition in Penaeid shrimp. *Journal of food science*, 86 (7): 312-320.

Snellings, S. L.; Takenaka, N. E.; Kim, H.Y. and Miller, D. W. (2003) : Rapid colorimetric method to detect indole in shrimp with gas chromatography Mass Spectrometry Confirmation. *Journal of food science*, 68(4):1548-1553.

Amine, M. T. (2003) : Quality of fresh and frozen shrimp in Alexandria city. The third international scientific conference. Mansoura, 29-30 April, 2003.

Khansari, F. E.; Ghazi-Khansari, M. and Abdollahi, M. (2005) : Heavy metals content of canned tuna fish. *Food Chem.*, 93:293-296.

Rogério Men., des, Amparo Gonçalves, José Pestana and Carla Pestana (2005) : Indole production and deepwater pink shrimp (*Parapenaeus longirostris*) decomposition. European Food Research and Technology Volume 221, Numbers 3-4 / August, 2005.

Cámara, F.; Amaro, M. A.; Barbera, R.; and Clemente, G. (2005) : Bioaccessibility of minerals in school meals: Comparison Between dialysis and solubility methods. Food Chem., 92: 481-489.

Cabrera T., Cabrera G., Rosas J., Velásquez A. and Silva M. (2005) : [Variation of the lipids and fatty acids in marine shrimps consumed in Venezuela] (Journal Article) Arch Latinoam Nutr Jun; 55(2):194-200.

Ibrahim, M. K. (2008) : Chemical indicators of sea food spoilage. Assiut Vet. Med. J. vol.51(107):67-93.

Thanonkaew, Benjakul A., S. and Visessanguan, W. (2006) : Chemical composition and thermal property of cuttlefish (*Sepia pharaonis*) muscle. J. Food Composition Analysis, 19(2-3): 127-133.

Judith, K.; Laurie, J. and Panunzio, J. (2006) : Cholesterol and Fatty Acids In Several Species of Shrimp Journal of Food Science Volume 54 Issue 2, Pages 237 - 239.

Yanar, Y. and Celik, M. (2006) : Seasonal amino acid profiles and mineral contents of green tiger shrimp (*Penaeus semisulcatus*, De Haan, 1844) and speckled shrimp (*Metapenaeus monoceros*, Fabricius, 1789). from the Eastern

Mediterranean Sea. Food Chem., 94: 33-36.

Erkan, N. and Ozden, O. (2007) : Proximate composition and mineral contents in aqua cultured sea bass (*Dicentrarchus labrax*), sea bream (*Spams aurata*) analyzed by ICP-MS. Food Chem., 102(3): 721-725.

Pisal Sriket, Soottawat Benjakul, Wonop Visessanguan and Kongkarn Kijroongrojana (2007) : Comparative studies on chemical composition and thermal properties of black tiger shrimp (*Penaeus monodon*) and white shrimp (*Penaeus vannamei*) meats. Food Chemistry Volume 103, Issue 4, Pages 1199-1207.

Gokoglu, N.; Yerlikaya, P. and Gokoglu, M. (2006) : Mini- Review. Trace elements in edible tissue of three shrimp species (*Penaeus semisulcatus*, *Parapenaeus longirostris* and *Palaemon serratus*). J. Sci. Food Agric., 88 : 175-178.

Kavun., V. Y., (2008) : Content of Microelements in the Grass Shrimp *Pandalus kessleri* (Decapoda: Pandalidae) from Coastal Waters of the Lesser Kurilskaya Ridge. Russian journal of marine biology Vol. No. 1.:64-72.

Abu Bakar, F.; Salleh, A. B.; Razak, C. N. A.; Basri, M.; Ching, M. K. and Son, R. (2006) : Biochemical Changes of Fresh and Preserved Freshwater prawn (*Macrobrachium rosenbergii*) During Storage. International Food Research Journal, (15), 2 | 81-191

Whithney, E. and Rolfe, S. R. (2008) : Understanding Nutrition (11th Edn. for international student nutrition), USA, pp: 410.

Abdullah Oksuz, Layse Ozyilmaz, ^evlut Aktas, ^ozde Gercek and zJelena Motte (2009) : A Comparative Study on Proximate, Mineral and Fatty Acid Compositions of Deep Seawater Rose Shrimp

(*Parapenaeus longirostris*, Lucas 1846) and red shrimp (*Plesionicea martia*, A. Edwards 1883). *Journal of Animal and Veterinary Advances* 8 (1) : 183-189, ISSN : 1680-5593.

الملخص العربى

الجودة الكيميائية للجمبرى المجدد الكامل والمنزوع الراس والمقشر

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لقد تم جمع ٧٥ عينة من الجمبرى المجدد الكامل والمنزوع الراس والمقشر من السوبر ماركت المختلفة بمحافظة الإسكندرية وذلك لتقييم الجودة الكيميائية وتشمل متوسط تركيز الأس الهيدروجينى ومتوسط النتروجين الكلى المتصاعد ومحتوى البروتين الكلى وكذلك محتوى الأندول والكوليسترول وتركيب الأحماض الدهنية والرقم الحمضى والأحماض الدهنية الحرة وكذلك مؤشرات تأكسد الدهون الابتدائية (CD) والثانوية (TBA) ومحتوى الدهون الكلية وكذلك محتوى المعادن مثل المنجنيز والنحاس والكاديوم وغيرها، وكذلك متوسط تركيز حمض البوريك، وقد أوضحت الدراسة النتائج الآتية : أعلى قيمة لمتوسط تركيز الأس الهيدروجينى والنتروجين الكلى المتصاعد والأندول والكوليسترول فى الجمبرى المقشر المجدد بمتوسط تركيز 6.5 ± 0.272 و 30.0 ± 0.218 على التوالى) وفى حالة تركيب الأحماض الدهنية كان أعلى متوسطات تركيزات للأحماض الدهنية الكلية المشبعة والغير مشبعة فى الجمبرى المجدد الكامل 41.802 ± 1.127 و 61.485 ± 2.211 على التوالى). بينما كان أعلى تركيز للأحماض الدهنية الأوميغا ٣ الكلية الغير مشبعة فى الجمبرى المنزوع الراس (5.773 ± 1.452) كما أظهرت الدراسة أن أعلى قيمة لمتوسط تركيز الرقم الحمضى (5.342 ± 0.312) والأحماض الدهنية الحرة (2.671 ± 0.235) كانت فى الجمبرى المقشر والكامل بالراس على التوالى وفى حالة مؤشرات تحليل الدهون الابتدائية (CD) والثانوية (TBA) كان أعلى تركيز فى الجمبرى المنزوع الراس 0.921 ± 0.092 و 0.04 ± 0.832 على التوالى، وقد أوضحت الدراسة أيضاً أن أعلى محتوى للمنجنيز والنحاس والزنك والكاديوم 76.45 p.p.m., 0.129 p.p.m., 0.259 p.p.m., 1.225 p.p.m. على التوالى كان فى الجمبرى المجدد الكامل بالراس، وفى حالة الحديد كان أعلى متوسط تركيز $(39$ p.p.m.) فى الجمبرى المنزوع الراس أما بالنسبة للصدويوم والبوتاسيوم فكان أعلى تركيز 200 p.p.m. و 650 p.p.m. فى الجمبرى المقشر، كما أشارت الدراسة أيضاً إلى أن متوسطات تركيزات المعادن الثقيلة مثل الكاديوم والرصاص والزنك كانت فى الحدود المسموح بها وكذلك متوسط تركيز حمض البوريك كان فى الحدود المسموح بها فى جميع العينات موضع الدراسة.