



International Journal of Fisheries and Aquatic Studies

E-ISSN: 2347-5129

P-ISSN: 2394-0506

(ICV-Poland) Impact Value: 5.62

(GIF) Impact Factor: 0.549

IJFAS 2019; 7(1): 243-248

© 2019 IJFAS

www.fisheriesjournal.com

Received: 01-11-2018

Accepted: 05-12-2018

Enenwa AA

Department of Biological
Sciences, Ahmadu Bello
University, Zaria, Nigeria

Suleiman B

Department of Biological
Sciences, Ahmadu Bello
University, Zaria, Nigeria

Abolude DS

Department of Biological
Sciences, Ahmadu Bello
University, Zaria, Nigeria

Biochemical qualities of three imported frozen fish species sold in Zaria, Nigeria

Enenwa AA, Suleiman B and Abolude DS

Abstract

The knowledge of fish and associated biochemical activity, likely to cause spoilage of the fish is paramount; and most of the fishes consumed by Nigerians are imported. Thus, there is a need to investigate the biochemical qualities of imported frozen fishes. This study was aimed to determine the biochemical qualities of three imported frozen fish species sold in Zaria, Nigeria. The biochemical qualities assessment of the fishes was conducted according to the methods of Riquixo (1998), Undeland *et al.* (2005) and Vyncke (2006). The result in *Sardina pilchardus*, *Trachurus trachurus* and *Clupea harengus*, showed a significant difference. This study revealed that total volatile nitrogen, thiobarbituric acid and peroxide value mean concentrations of 22.87, 1.94 and 4.18, respectively in the three fish species are within the acceptable limit, except trimethylamine amine (12.88) which is not within the acceptable limit. Therefore, the biochemical qualities of imported frozen *Clupea harengus*, *Sardina pilchardus* and *Trachurus trachurus* sold in Zaria is slightly not suitable for human consumption.

In conclusion, TVN, TBA, and TMA concentrations in the three fish species are within the acceptable limit of FAO. Therefore, the biochemical qualities of imported frozen *C. harengus*, *S. pilchardus* and *T. trachurus* sold in Zaria are suitable for human consumption.

Relevant agencies should ensure strict compliance to recommended biochemical limits of frozen fish imported into Nigeria.

Keywords: biochemical qualities, fish species, imported

Introduction

Fish is the cheapest animal protein source and it is being used increasingly because of its availability, palatability and health provisions^[1, 2]. Fish and fish products are known worldwide as a very important diet because of their high nutritive quality and significance in improving human health. Fish plays a vital role in feeding the world's population and contributing significantly to the dietary protein intake of hundreds of millions of the people. On a global scale, almost 16% of total average intake of animal protein was attributable to fish in 1988^[3].

Biochemical studies of fish tissue are of considerable interest for their specificity in relation to the food values of the fish and for the evaluation of the physiological needs at different periods of the fish life cycle. Changes in chemical composition of body have been known to reflect storage or depletion of energy reserves. The values of body composition in fishes vary considerably within and between species, with fish size, sexual condition, feeding, time of the year and activity^[4]. Biochemical tests have been used to establish quantities of different spoilage compounds in fish. Fish are highly perishable, and prone to vast variation in quality due to difference in species, environmental and feeding habitats and action of autolysis on the fish muscle^[5]. Marketing of frozen fish in Nigeria is mostly carried out by local fish sellers who have little or no knowledge of temperature fluctuations. Therefore, knowledge of the fish and associated biochemical activity likely to cause spoilage of the fish is paramount, thus there is an immense need to investigate the biochemical qualities of imported frozen fish.

Materials and Methods

Source of fish sample

Marine fish types that were used in this study include *C. harengus* (also known as herring or *Shawa* in south western Nigeria), *S. pilchardus* (Sardine) and *T. trachurus* (also known as horse mackerel or *kote* in south western Nigeria). The table-size fishes were purchased from the fish depot located at Sabon Gari, Zaria, Kaduna state, Nigeria of latitude 11.1231°N and

Correspondence

Enenwa AA

Department of Biological
Sciences, Ahmadu Bello
University, Zaria, Nigeria

longitude 7.7322°E. These fishes were chosen because they are readily available and their affordability cuts across the various economic classes of Nigeria. The three imported frozen fish species (*Clupea harengus*, *Sardina pilchardus* and *Trachurus trachurus*) were purchased from the fish depot located at Sabon gari, Zaria, Kaduna state, Nigeria.

Identification and preparation of fish samples

The fish were immediately brought in ice boxes to the Fisheries Laboratory, Department of Biological Science, Ahmadu Bello University, Zaria. The collections were carried out in such a way that from 20 fish samples, 2 pooled samples of fish was drawn. Collection was carried out thrice. A total of 60 fishes per species were collected for analysis. The fish species were identified as *C. harengus*, *S. pilchardus* and *T. trachurus* using the keys of [6, 7]. Weight was measured in grams, using Sartorius CP820 model, while the standard length and total length in centimetres were measured with the aid of a measuring board. The fish samples were gutted, beheaded, filleted, thoroughly rinsed with distilled water and kept in air-tight labelled plastic container and stored at freezing temperature of 0 °C to -4 °C

Biochemical methods of fish quality assessment

Determination of peroxide value (PV)

Two grams of each fish sample was dissolved in 10 ml chloroform and 30 ml glacial acetone saturated potassium iodide was added. The samples were kept for 30 minutes to enable adequate reaction with the chemical. 20 ml of 5% KI was then added, followed by 3 drops of starch solution. The solution containing the sample was then titrated with 0.1 N sodium thiosulphate. Colour changes from dark brown to white after titration. Blank samples were prepared using the above procedure but without the sample.

PV was determined using the published ferric thiocyanate method [8].

PV will be calculated by the following equation:

$$PV \text{ (mEq peroxide kg}^{-1}\text{)} = \frac{(A \text{ sample} - B \text{ blank}) \times 0.1N \times 1000}{W}$$

Where,

W = weight of sample in grams

0.1 N = Concentration of sodium thiosulphate

Determination of thiobarbituric acid (TBA)

Thiobarbituric acid (TBA) was determined according to the method of [9]: 10 grams of fish flesh was homogenised with 50 ml of 7.5% trichloroacetic acid for one minute using an electric blender. The mixture was filtered using Whatman No1 filter paper. The filtrate was distilled until 50 millilitres of distillate was obtained. Five millilitres of thiobarbituric acid reagent (0.02 M of 2-thiobarbituric acid in distilled water) was added to five millilitres distillate and five millilitres distilled water in a test tube. Five millilitres TBA reagent and five millilitres distilled water were used for the blank. The test-tubes were covered using screw caps and further placed at 90 °C in a water bath for 40 minutes, after

which the test tubes were cooled under tap water. The absorbance was measured at 538 nm using Jenway 6405 uv/vis. The optical density of the diluted solution was measured with a spectrophotometer.

TBA (mg malonaldehyde kg⁻¹) = Absorbance value of sample x 7.8.

Determination of Total Volatile Nitrogen

Total volatile nitrogen was determined by using trichloroacetic (TCA) extract steam distillation method¹⁰: 50 ml of 7.5% aqueous TCA solution was added to 25 g of fish muscle and was then homogenised for 1 minute using an electric blender, the mixture was filtered using Whatman no 1 filter paper. 25 ml of filtrate was then loaded into the distillation tube followed by 6 ml of 10% NaOH. A beaker containing 15 ml of 4% boric acid and 2 drops of methyl red indicator was placed under the condenser until 100ml of the distillate was obtained after distillation. The boric acid solution was titrated with 0.03 N sulphuric acid solution using a graduated burette. The colour changed from grey to red. The quantity of TVN in mg was determined from the volume of sulphuric acid (ml) obtained after titration.

The TVN mg-N/100g will be determined using following calculation

$$TVN \text{ mg-N/100g} = \frac{(A) (0.055 \text{ mol/l}) (14 \text{ N/mol}) 100}{8.333}$$

A = amount of sulphuric acid used

14 = Molar mass of nitrogen

Determination of Trimethylamine by picric acid method (TMA)

Trimethylamine was determined using picric acid method¹⁰: Trimethylamine (TMA) standard stock solution was prepared by adding 0.7ml of TMA was added to 1 ml of HCl and diluted to 100 ml with distilled water using a volumetric flask. Working solution was prepared by adding 1ml stock solution to 1ml HCl and it was then diluted to 100 ml with distilled water in a volumetric flask. Out of the working solution, 4ml of distilled water was used as blank for TMA standard. For the standard 1 ml, 2 ml and 3 ml of working solutions were used and diluted to 4 ml with distilled water. Absorbance was read at 410 nm. 40 ml of 7.5% trichloroacetic acid aqueous solution was added to 20 g of each fish sample and blended for 1min using an electric blender. The mixture was filtered using Whatman no 1 filter paper to receive clear solution. 1 ml sample, 3 ml distilled water, 1 ml 20% formaldehyde, 3 ml 45% KOH and 10 ml clean toluene were put into a reagent glass. The reaction glass was shaken 10 times. 7-8 ml of solution was decanted using pump pipette and introduced to second glass containing 0.3 g of dry Na₂SO₄. The mixture was shaken for 15 mins at 3rps using Gallen kamp flask shaker machine. 4 ml of the solution was put into new reagent glass containing 4 ml of 0.2% picric acid. The TMA in mg-N/100 g was determined using following calculation:

$$TMA \text{ mg-N/ml standard solution} = \frac{\text{Concentration of standard}}{\text{Absorbance of standard}} \times \text{Volume of standard}$$

TMA mg-N/100 g sample = (A-B) x 3 x TMA mg-N/100 standard x C

A = Absorbance of the sample

B = Absorbance of blank

C = Dilution of sample

Statistical analysis

Data was subjected to one-way analysis of variance (ANOVA) by using the general linear model procedure. Differences between sample means were present, were ranked using Duncan range multiple test. The values at $P \leq 0.05$ were considered statistically significant.

Results

Analysis of the Biochemical Qualities of *C. harengus*, *S. pilchardus* and *T. trachurus*

Total volatile nitrogen (TVN)

In *S. pilchardus*, the TVN value within the samples collected showed significant difference ($P \leq 0.05$). The third collection showed the highest TVN value of 40.20 mg-N/100g which indicates that it was spoilt according to the quality index. The first and second collections were very good according to the quality index, the TVN value of the first and second collections are 9.24 mg-N/100 g and 19.17 mg-N/100 g respectively which indicate that they were very good according to the quality index (Table 1).

In *C. harengus*, the mean of the TVN value within the samples collected were significantly different ($P \leq 0.05$). The third collection had the highest value of TVN 55.44 mg-N/100 g which indicates that the third collection was spoilt according to the quality index. The first and second collection with TVN values of 8.78 mg-N/100 g and 17.10 mg-N/100 g respectively indicates that they were very good. The first collection has the lowest TVN value (Table 1).

In *T. trachurus*, the TVN values within the collection samples were highly significantly different ($P \leq 0.05$). The second collection had the highest TVN value of 24.49 mg-N/100 g, while the first and third collections had 9.47 mg-N/100 g and 21.95 mg-N/100 g respectively. According to the quality index, all the *T. trachurus* samples collected were very good (Table 1).

The TVN values of each fish species are not significantly high as shown in Table 5, although that of *Trachurus trachurus* is the best because it has the lowest TVN value of 18.65 mg-N/100 g.

Trimethylamine (TMA)

In *S. pilchardus*, the TMA value within the samples collected was significantly high. The highest value of TMA was observed in the third collection 20.77 mg-N/100 g, while the lowest is the second collection 6.55 mg-N/100 g. The first collection had TMA value of 10.62 mg-N/100 g as shown in Table 2.

In *C. harengus*, the samples collected had highly significant TMA values. The third collection had the highest TMA value of 40.67 mg-N/100 g, while the first collection had the lowest TMA value of 2.13 mg-N/100 g. The second collection had TMA value of 3.37 mg-N/100 g as shown in Table 2.

The TMA value within the *T. trachurus* samples collected was significant. The third collection had the highest TMA value of 2.64mg-N/100 g while the second collection had the lowest value of 1.39 mg-N/100 g as shown in Table 2.

The TMA values for each fish species indicate that the quality is spoilt for *S. pilchardus* and *C. herangus* but *T. trachurus* is

marketable as shown in Table 5.

Peroxide value (PV)

In *S. pilchardus*, the PV for the samples collected was significantly high. The third collection had the highest PV value of 8.80 meq/kg, indicating that it is above limits according to the quality index. The first collection had the lowest PV of 2.40 meq/kg as shown in Table 3.

In *C. harengus*, the PV for the sample collected is not significantly different. The first collection had the highest PV of 4.00 meq/kg indicating that it was very good according to the quality index and the lowest value was observed in the 1.75 meq/kg which was the second collection as shown in Table 3.

The PV values for each of the three fish species indicate that the quality is good, although *C. herangus* has the least value as shown in Table 3. The PV value among the three fish species is not significantly high at $P > 0.05$.

In *T. trachurus*, the PV for the sample collected is showed significant difference at $P \leq 0.05$. The first collection had the highest PV of 7.20 meq/kg while the lowest PV value was 2.85 meq/kg observe in the second collection as shown in Table 3.

Thiobarbituric acid (TBA)

In *S. pilchardus*, the TBA values for the collected samples were significantly high. The third collection had the highest TBA value of 3.71 mg/kg indicating that it was very good according to the quality index meanwhile the first collection had the lowest TBA value of 0.50 mg/kg indicating that it was very good according to the quality index. The second collection had TBA value of 1.44 mg/kg indicating that it was also very good according to the quality index as shown in Table 4.

In *C. harengus*, the TBA values for the collected samples showed significant difference at $P \leq 0.05$. The third collection had the highest TBA value of 4.00 mg/kg indicating that it was very good according to the quality index while the first collection had the lowest TBA value of 0.90 mg/kg indicating that it was very good according to the quality index shown in Table 4.

In *T. trachurus*, the TBA values for the collected samples were not significantly different at $P \leq 0.05$. The third collection had the highest TBA value of 2.82 mg/kg indicating that it was very good according to the quality index while the first collection had the lowest TBA value of 0.39 mg/kg indicating that it was very good according to the quality index as shown in Table 4.

The TBA values for each of three fish species indicate that the quality is very good, although *T. trachurus* has the least value of 1.51 mg/kg as shown in Table 4.

Discussion

During the present study, 60 *C. herangus* was analysed with an average weight of 274 g (range 176.9-262.1 g), and 60 *S. pilchardus* with an average weight of 353.93 g (range 224.9-507.4 g) and 60 *T. trachurus* with an average weight of 523.23 g (range 423.8-602.5 g).

The biochemical quality differ from one fish to the other and improper handling of fish and part of the preservation processes leads to fish spoilage. The stressful environment in which the frozen fish undergoes the long distant journey from India, Germany or China to Zaria could inhibit the freshness of the fish because: breakdown of the freezer and improper

trans-loading.

Total Volatile Nitrogen (TVN)

The results of this project have shown in the 1st and 2nd collections of *S. pilchardus* that the TVN are within acceptable limit except the 3rd collection which exceeded the acceptable limit. The acceptable limit of TVN in *S. pilchardus* is ≤ 25 -35 mg-N/100g.

The results of this project have shown in the 1st and 2nd collections of *C. harengus* that the TVN are within acceptable

limit except the 3rd collection which exceeded the acceptable limit. The acceptance limit of TVN in *C. harengus* is ≤ 25 -35 mg-N/100 g. But in *T. trachurus* all the three collections are within the acceptable limit. The acceptable limit of TVN in *T. trachurus* is ≤ 25 -35 mg-N/100. There were significantly high differences within the three fish species which may lead to N-nitroso-compound (NOC) induced cancer, diarrhea and it can also trigger respiratory conditions ranging from asthma to even death [5].

Table 1: TVN within Three Collections of Each Species (*Clupea harengus*, *Sardina pilchardus* and *Trachurus trachurus*)

Collection	<i>Sardine pilchardus</i>	Quality Index	<i>Clupea harengus</i>	Quality Index	<i>Trachurus trachurus</i>	Quality Index
1 st	9.24 ± 0.53 ^c	Very good	8.78 ± 1.10 ^b	Very good	9.47 ± 1.27 ^b	Very good
2 nd	19.17 ± 1.02 ^b	Very good	17.10 ± 1.22 ^{ab}	Very good	24.49 ± 1.22 ^a	Very good
3 rd	40.20 ± 1.39 ^a	Spoilt	55.44 ± 21.10 ^a	Spoilt	21.95 ± 2.60 ^a	Very good
P value	0.000**		0.050*		0.001**	

**= highly significant. *= significant. Means with the same superscript are not significantly different ($P \leq 0.05$).

Table 2: TMA within Three Collections of Each Species (*Clupea harengus*, *Sardina pilchardus* and *Trachurus trachurus*)

Collection	<i>Sardine pilchardus</i>	Quality Index	<i>Clupea herangus</i>	Quality Index	<i>Trachurus trachurus</i>	Quality Index
1 st	10.62 ± 0.07 ^{ab}	Marketable	4.37 ± 0.67 ^b	Marketable	1.80 ± 0.15 ^b	Very Good
2 nd	6.55 ± 1.33 ^b	Marketable	3.37 ± 1.60 ^b	Good	1.39 ± 0.29 ^b	Very Good
3 rd	20.77 ± 2.62 ^a	Spoilt	40.67 ± 3.53 ^a	Spoilt	2.64 ± 0.03 ^a	Very Good
P value	0.001**		0.002**		0.000**	

*= significant. **= highly significant. Means with the same superscript are not significantly different ($P \leq 0.05$).

Table 3: PV within Three Collections of Each Species (*Clupea harengus*, *Sardina pilchardus* and *Trachurus trachurus*)

Collection	<i>Sardine pilchardus</i>	Quality Index	<i>Clupea herangus</i>	Quality Index	<i>Trachurus Trachurus</i>	Quality Index
1 st	2.40 ± 0.46 ^b	Good	4.00 ± 0.92 ^a	Good	7.20 ± 0.81 ^a	Good
2 nd	2.55 ± 0.32 ^b	Good	1.75 ± 0.18 ^b	Good	2.85 ± 0.75 ^b	Good
3 rd	8.80 ± 0.00 ^a	Spoilt	2.40 ± 0.46 ^{ab}	Good	4.00 ± 0.69 ^b	Good
P value	0.000**		0.068ns		0.007**	

Means with the same superscript are not significantly different ($P \leq 0.05$).

Table 4: TBA within Three Collections of Each Species (*Clupea harengus*, *Sardina pilchardus* and *Trachurus trachurus*)

Collection	<i>Sardine pilchardus</i>	Quality Index	<i>Clupea herangus</i>	Quality Index	<i>Trachurus trachurus</i>	Quality Index
1 st	0.50 ± 0.02 ^b	Very Good	0.90 ± 0.06 ^b	Very Good	0.39 ± 0.03 ^a	Very Good
2 nd	1.44 ± 0.43 ^b	Very Good	2.42 ± 0.12 ^{ab}	Very Good	1.33 ± 0.08 ^a	Very Good
3 rd	3.71 ± 0.84 ^a	Very Good	4.00 ± 1.38 ^a	Very Good	2.82 ± 1.37 ^a	Very Good
P value	0.007**		0.046*		0.15ns	

**= highly significant *=significant. Means with the same superscript are not significantly different ($P \leq 0.05$).

Table 5: Comparative Analysis of the Biochemical Qualities among *Clupea harengus*, *Sardina pilchardus* and *Trachurus trachurus*

Species	TVN	Quality Index	TMA	Quality Index	PV	Quality Index	TBA	Quality Index
<i>Sardina pilchardus</i>	22.87 ± 3.93 ^a	Very Good	12.64 ± 2.01 ^a	Spoilt	4.18 ± 0.78 ^{ab}	Good	1.88 ± 0.50 ^a	Very Good
<i>Clupea harengus</i>	27.10 ± 8.85 ^a	Good	16.12 ± 5.29 ^a	Spoilt	2.72 ± 0.43 ^b	Good	2.44 ± 0.54 ^a	Very Good
<i>Trachurus trachurus</i>	18.64 ± 2.19 ^a	Very Good	9.87 ± 3.54 ^a	Marketable	4.68 ± 0.68 ^a	Good	1.51 ± 0.51 ^a	Very Good
mean	22.87	Very Good	12.88	Spoilt	4.18	Good	1.94	Very Good
P value	0.58ns		0.52ns		0.10ns		0.45ns	

ns =not significant at 95% confident limits. Means with the same superscript are not significantly different ($P \leq 0.05$).

Trimethylamine (TMA)

The present results indicate that the concentrations of TMA in the 1st and 2nd collections of *S. pilchardus* were within acceptable limit except the 3rd collection which exceeded the acceptable limit. The acceptable limit of TMA in *S. pilchardus* is ≤ 10 mg/100 g. The results of this project have shown in the 1st and 2nd collections of *C. harengus* that the TMA are within acceptable limit except the 3rd collection which exceeded the acceptance limit. The acceptance limit of TMA in *C. harengus* is ≤ 10 mg/100 g. In *T. trachurus* all the three collections are within the acceptance limit. The acceptance limit of TMA in *T. trachurus* is ≤ 10 mg/100 g. There was

highly significant difference in TMA level among the collected samples of *S. pilchardus*, *T. trachurus* and *C. harengus*.

The amount of TMA produced is a measure of the activity of spoilage bacteria in the fish flesh and so it's an indicator of spoilage. The increase in the amount of TVN parallels the increase in TMA. The TMA value states the level of spoilage before freezing [11].

Peroxide Value (PV)

The results indicate that the PV in the 1st and 2nd collections of *S. pilchardus* was within acceptable limit except the 3rd

collection which exceeded the acceptable limit. The acceptable limit of PV in *S. pilchardus* is ≤ 8 meq/kg. The results of this project have shown that in all the three collections of *C. harengus* that the PV is within acceptable limit. The acceptance limit of PV in *C. harengus* is ≤ 8 meq/kg. The results indicate that in *T. trachurus* all the three collections are within the acceptable limit. The acceptable limit of PV in *T. trachurus* is ≤ 8 meq/kg. The PV within *S. pilchardus* and *T. trachurus* indicates that it is highly significant, while that of *C. harengus* indicates that they are not significantly different at $P > 0.05$.

Oxidation of the oil in oily fish (*C. harengus*) gives rise to rancid odour and flavor which limit the storage life of these fish species more quickly. Increase in the peroxide value is most useful as an index of earlier stage of oxidation; as oxidation proceeds the peroxide value starts to fall [12].

Thiobarbituric Acid (TBA)

The results indicate that the concentrations of TBA in all the three collections of *S. pilchardus* were within acceptable limit. The acceptance limit of TBA in *S. pilchardus* is ≤ 8 mg/kg. The results indicate that the concentrations of TBA in all the three collections of *C. harengus* were within acceptable limit. The acceptance limit of TBA in *C. harengus* is ≤ 8 mg/kg. The results indicate that the concentrations of TBA in all the three collections of *T. trachurus* were within acceptable limit. The acceptable limit of TBA in *T. trachurus* is ≤ 8 mg/kg. The P values within *S. pilchardus*, *C. harengus* and *T. trachurus* indicate that they are not significant. Increase in TBA value was the measure of the extent of oxidative deterioration in oily fish (herring) as in the case of peroxide value which could also fall at the later stage of spoilage [13].

Comparative Analysis Among The Three Species

Among the three species used for this project, there was no significant difference with any of the four parameters (TVN, TMA, PV and TBA) in the experiments. Although *C. harengus* had the highest values, followed by *S. pilchardus* and *T. trachurus* in three (TVN, TMA, and TBA) out of the four parameter. The reasons could be that the lower the weight the higher the value of TVN, TMA, and TBA. In PV, the reverse was the case whereby *T. trachurus* had the highest value, followed by *S. pilchardus* and thirdly, *C. harengus*. The reason could be that the higher the fish weight the higher the PV (meq/kg). High TVN and TMA concentrations could be as a result of fish handling after catch and the seawater showers defrosting method, with the addition of storage time for these species. [14] found that TVN and TMA quantities accumulate rapidly at ambient temperature (21 °C –27 °C) in the flesh of frozen sardines and reach values of 11.2 mg TMA/ 100 g and 57.5 mg TVB/ 100 g. [15] found that the growth of the same parameters in two experiments done with frozen sardines was rapid, reaching 2.72 mg TMA/100g and 5.20 mg TVN/ 100 g of sardine flesh per day. TMA quantities depend on the condition of individual fish before catch, season, handling after catch, freezing method and storage time; these could be possible causes for the variations and differences among individual samples.

Low TVN and TMA values in *Trachurus trachurus* samples were detected while in fish stored for a longer period at -18°C, growth of the volatile amines was present. If kept at room temperature after defrosting, TMA and TVB quantities in fish would increase over the limit of tolerance within a few hours.

These values continue as a linear growth [16]. Studies have shown that TVN quantities above the limit of acceptance do not always follow at the beginning of the spoilage process [17]. The increase of TVN quantities in fish controls the exponential growth of the TMA concentration; the spoilage process was considered present when TMA in the fish crosses the limit of acceptance [18, 19] have stated that storage of any kind increases TVN values and when those values reach the highest level of tolerance (25–35 mg / 100g) the fish is considered spoiled due to increased bacterial activity.

The Speed of deterioration can be linked to the history of the fish before freezing, where metabolism has initiated the process that progresses more rapidly when defrosted than it should when freezing was done immediately and the storage was correct.

Protein requirements generally are higher for smaller fish. As fish grow larger, their protein requirement usually decrease; protein requirements also vary with rearing environmental water temperature and water quality, as well as the teaching rules of the fish. (FAO, 1996)

Decrease in TBA values indicated decrease in level of lipid oxidation in fish [20].

Increase of TVN can be attributed to a decreasing trend of volatile nitrogen analyser enzymes or a decreasing amount of a substrate such as trimethylamine or dimethylamine or non-protein nitrogen. [21, 22] have reported that samples could be considered consumable if the TVN level is less than 20 mg/100 g fish and that a level of more than 30 mg determines the product as not consumable. The increasing of TVN value during storage is related to bacterial spoilage and activity of endogenous enzymes [23].

Decrease of TBA values in fish could be attributed to the interaction of decomposition products of protein with malonaldehyde to give tertiary products [24].

Increase in the peroxide value of the fish during frozen storage might be due to mechanical mincing of fish meat which accelerates oxidation due to the incorporation of oxygen in the tissue or the disruption and intermixing of tissue components. A similar increase in the PV content was observed by [25].

In conclusion, this study revealed that TVN, TBA, and TMA concentrations in the three fish species are within the acceptable limit of FAO. Therefore, the biochemical qualities of imported frozen *C. harengus*, *S. pilchardus* and *T. trachurus* sold in Zaria are suitable for human consumption.

References

1. Azam K, Ali MY, Asaduzzaman M, Basher MZ, Hossain MM. Biochemical assessment of selected fresh fish. Journal of Biological Science. 2004; 4(1):9-10.
2. Akinwumi FO. Bioefficacy of some oil-mixed plant derivatives against African mud catfish (*Clarias gariepinus*) beetles, *Dermestes maculatus* and *Necrobia rufipes*. Journal of Agricultural Technology. 2011; 7(2):369-381.
3. Food and Agricultural Organization Commodity Review and Outlook. FAO, Rome, 1990.
4. Saliu JK. Effect of smoking and frozen storage on the nutrient composition of some African fish. Advance National Applied Science. 2008; 2(1):16-20.
5. Venugopal V. Biosensors in fish production and quality control. Biosensors and bioelectronics. 2002; 17:147-157.
6. Burchard AJ, Reed WJ, Hopson J, Yaro I. *Fish and Fisheries of Northern Nigeria*. Published by Ministry of

- Agriculture, Northern Nigeria. Sokoto, 1967.
7. Froese R, Pauly D. Fish Base: World Wide Web electronic publication, 2012. <http://www.Fishbase.org>
 8. Undeland IG, Hall K, Wendin I, Gangby, Rutgersson A. Preventing lipid oxidation during recovery of functional proteins from herring (*Clupea harengus*) fillets by an acid solubilisation process. Agricultural Food Chemistry journal. 2005; 53:5624-5634.
 9. Vyncke W. Direct determination of the thiobarbituric acid value in trichloroacetic acid extracts of fish as a measure of oxidative rancidity. European Journal of Lipid Science and Technology. 2006; 72(12):1084-1086
 10. Riquixo C. Evaluation of Suitable Chemical Methods for Seafood Products in Mozambique. United Nation University, Iceland, 1998, 27-28.
 11. Food and Agricultural Organization Fisheries Technical papers no 480/1 Promotion of Sustainable Commercial Aquaculture in Sub-Saharan Africa. Policy Framework, 2001, 1
 12. Food and Agricultural Organization Quality and Quality Changes in Fresh Fish. Rome, Italy, 1995.
 13. Ababouch LH, Souibri L, Rhaliby K, Ouahdi O, Battal M, Busta FF. Quality changes in sardines (*Sardina pilchardus*) stored in ice and at ambient temperature. Food Microbiology. 1996; 13:123-32.
 14. Ruiz-Cappillas C, Jimenez-Colmenero F. Biogenic amines in meat and meat products. Crit Review Food Science and Nutrient. 2004; 44:489-499.
 15. Fitzgerald CH, Bremner HA. Improving the Stability and Nutritional Value of Frozen Small Fish for Tuna Feed. In: Aquafin CRC Final report. Australia Fisheries Research Development Corporation, Adelaide. 1994, 36
 16. Shakila RJ, Vijayalakshmi K, Jeyasekaran G. Changes in histamine and volatile amines in six commercially important species of fish of the Thoothukkudi coast of Tamil Nadu, India stored at ambient temperature. Food Chemistry. 2003; 82:347-352.
 17. Ozogul F, Taylor KDA, Quantick P, Ozogul YO. Biogenic amines formation in atlantic herring (*Clupea Harengus*) stored under modified atmosphere packaging using a rapid GC/MS method. International Journal of Food and Science Technology. 2002; 37(35):515-522.
 18. Fraser OP, Sumar S. Compositional changes and spoilage in fish (part II) – microbiological induced deterioration. Nutritiona Food Science. 1998; 6:325-329.
 19. Food and Agricultural Organization. Microbiological spoilage of fish and fish products. Rome, Italy, 1996.
 20. Abramson H. Oxidation of unsaturated fatty acid in normal and scorbutic guinea pigs. Journal of Biological Chemistry. 1949; 178:179-183.
 21. Connell JJ, Shewan JM. Past, present and future of fish science. In Connell, J.J. ed. *Advances in Fish Science and Technology*. Jubilee conference of Torry Research, England, 1980.
 22. Pearson D. The Chemical Analysis of Foods. 6th Edn., Long Man Group Ltd., Safiyari Sh, Moradi, 1997.
 23. Chomnawang C, Nantachai K, Yongsawatdigul J, Thawornchinsombut S, Tungkawachara S. Chemical and biochemical changes of hybrid catfish fillet stored at 4 °C and its gel properties. Food Chemistry. 2007; 103:420-427
 24. Hernández-Herrero MM, Roig-Sagués AX, Rodríguez-Jerez JJ, Mora-Ventura MT. Total Volatile Basic Nitrogen and other Physico-chemical and Microbiological Characteristics as Related to Ripening of Salted Anchovies. Journal of Food Science. 1999; 64(2):344-347.
 25. Ninan G, Bind J, Joseph J. Frozen storage studies of value added mince based products from tilapia (*Oreochromis mossambicus*, Peters 1852). Journal of Food Process Preservation. 2010; 34:255-271