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Chemical quality of marketed fresh-water fish in Qalyuobia Governorate Egypt

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ABSTRACT

For determination of the changes in potential of hydrogen (pH), total volatile nitrogen (TVN) and trimethylamine (TMA) in three types of fish (Oreochromis niloticus, Clarias lazera and Mormyrus niloticus), 30 samples of each were collected from markets of Qalyuobia Governorate, Egypt. The results revealed that the mean value of pH in the examined samples were 6.36 ± 0.05, 6.19 ± 0.03 and 6.07 ± 0.02 for Oreochromis niloticus, Clarias Lazera and Mormyrus niloticus, respectively. The mean values of TVN were 21.58 ± 0.49 mg%; 16.73 ± 0.41 mg% and 14.15 ± 0.28 mg% for Oreochromis niloticus, Clarias Lazera and Mormyrus niloticus, respectively. The un-accepted samples were 16.67%, 6.67% and 3.33% in Oreochromis niloticus, Clarias lazera and Mormyrus niloticus, respectively. Trimethyl Amine values were 8.85 ± 0.22 mg% for Oreochromis niloticus, 6.61 ± 0.15 mg% for Clarias lazera and 5.97 ± 0.13 mg% for Mormyrus niloticus. The un-accepted samples were 20%, 13.33% and 3.33% in Oreochromis niloticus, Clarias lazera and Mormyrus niloticus, respectively.

1. INTRODUCTION

Fish is one of the most vital foodstuffs, easily digested and of high palatability. It is also known to have a higher food conversion rate than other meat type animals (Abdel Ghany, 2003). Furthermore, Fish oil represents a good source of calories and provides many important vitamins as B group, A and D, beside calcium, phosphorus and iodine (Feldhusen, 2000).

The four major constituents in the edible portion of fish meat are water, protein, lipid (fat or oil) and ash (minerals). The analysis of these four basic constituents of fish muscle is often referred to as 'proximate analysis'. Reliable data on proximate composition of most of the species of fish are difficult to obtain (Venugopal and Shahidi, 1996; Bandarra et al., 2009). So, pH, TVN and TMA tests are used to determine fish quality for human consumption.

Measuring of pH in Nile fish is very important as changes in the pH, especially sudden changes, can prove harmful effects on human health or even fatal to fish (Kelleher, 2004).

Total volatile nitrogen (TVN) consists mainly of trimethylamine (TMA) and ammonia (NH_3), is used as a quality criterion for fish meal raw material as they increased in case of fish spoilage. Trimethylamine analysis reflects only stages of advanced spoilage of fish, they are considered unreliable for the evaluation of the fish freshness in the early stage of storage (Baixas-Nogueras *et al.*, 2002).

So, the current study is performed for determination of changes in pH, TVN and TMA in three types of fish (*Oreochromis niloticus*, *Clarias lazera* and *Mormyrus niloticus*) as indicators of fish spoilage.

2. MATERIAL AND METHODS

2.1. Collection of samples:

A total of 90 random samples of Nile fish represented by *Oreochromis niloticus*, *Clarias lazera* and *Mormyrus niloticus* (30 of each) were collected from fish markets at Benha city, Qalyuobia Governorate. Each sample was kept in a separated plastic bag in an ice box, transferred to the laboratory without undue delay and examined as quickly as possible.

2.2. Keeping quality tests:

2.2.1. Determination of pH

Ten gm of the sample were blended in 10 ml of neutralized distilled water. The homogenate was left at room temperature for 10 minutes with continuous shaking. The pH value was determined by using an electrical pH meter (Bye model 6020, USA). Calibration of pH meter by using two buffer solutions of exactly known pH (alkaline pH 7.01, acidic pH 4.01). Therefore, pH electrode was washed with neutralized water and then introduced into the homogenate after the temperature correction system was adjusted (Pearson, 2006).

2.2.2. Determination of Total Volatile Nitrogen (TVN):

Total volatile nitrogen (TVN) was determined according to Food and Agriculture Organization (1980). Briefly, in a clean dry beaker, 10 gm of the sample were added to 30 ml of distilled water and thoroughly mixed by a

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blender for 2 minutes. Then, 2 drops of 0.02 M HCl were added to bring the pH value to 5.2. The homogenate was slowly heated to 70°C and then cooled to room temperature and filtered. Accurately, the outer ring was filled with 2 ml of the sample extract and 1 ml of saturated potassium carbonate (KCO_3). The Conway unit was rotated as gently as possible and the dish was covered and incubated at 36 °C for 2 hours, HCl in the inner ring was titrated against 0.01M NaOH by using methyl red indicator (T1 ml).

TVN/l00g = 26.88 × (2-T_1) Where, T_1 = volume of NaOH consumed in the titration.

2.2.3. Determination of Trimethylamine (TMA):

The method adopted by Food and Agriculture Organization (1980) was applied using Conway test. Briefly, 2 ml of 0.05 M H_2SO_4 were added into the inner compartment of Conway dish, however, the outer ring of the dish was filled with 2 ml of the sample extract and 1 ml of saturated potassium carbonate (KCO_3). Furthermore, the dish was covered and incubated at 36°C for 2 hours. Then, H_2SO_4 in the inner ring was titrated against 0.01M NaOH by using methyl red indicator (T2 ml).

TMA/l00g = 26.88 × (2-T_2). Where, T_2 = volume of NaOH consumed in the titration.

4. Statistical Analysis:

Analysis of Variance (ANOVA) test was applied for statistical evaluation of the obtained results for each parameter according to Feldman et al. (2003).

3. RESULTS

3.1. pH value

Table (1) declared that the pH values in the examined fish samples were varied from 6.17 to 6.59 with an average of 6.36 ± 0.05 for *Oreochromis niloticus*, 6.08 to 6.51 with an average of 6.19 ± 0.03 for *Clarias lazera* and 5.94 to 6.33 with an average of 6.07 ± 0.02 for *Mormyrus niloticus*, respectively. The differences between the examined samples of three different fish species were significant (P<0.05) as shown in table (2). According to Egyptian Organization of Standardization and Quality "EOSQ" (2005) which recommended that the critical limits for pH should not be more than 6.2 in fish, the number of un-accepted samples are 3, 1 and 0 represented as 10%, 3.33% and 0% in *Oreochromis niloticus*, *Clarias lazera* and *Mormyrus niloticus*, respectively (Table 3).

3.2. Total Volatile Nitrogen value:

It was evident from results recorded in Table (4) that the TVN values in examined fish samples were varied from 9.23 to 35.68 with an average of 21.58 ± 0.49 mg% for *Oreochromis niloticus*, 5.56 to 29.10 mg% with an average of 16.73 ± 0.41 mg% for *Clarias lazera* and 4.92 to 26.47 mg% with an average 14.15 ± 0.28 mg% for *Mormyrus niloticus*, respectively. The differences between the examined different fish samples were highly significant (P<0.01) as shown in table (5). According to EOSQ (2005) which recommended that the permissible limit is 25 mg% for TVN, the number of un accepted samples are 5.2 and 1 represented as 16.67%, 6.67% and 3.33% in *Oreochromis niloticus*, *Clarias lazera* and *Mormyrus niloticus* respectively, so the all examined samples of fish based on their levels of TVN are acceptable as shown in Table (6).

3.3. Trimethyl amine value:

Table (7) ~~and Figure (5)~~ indicated that TMA values in three types of different fish samples were varied from 5.16 to 14.71 mg% with average 8.85 ± 0.22 mg% for *Oreochromis niloticus*; 3.84 to 11.02 mg% with an average 6.61 ± 0.15 mg% for *Clarias lazera* and 3.19 to 10.35 mg% with an average 5.97 ± 0.13 mg% for *Mormyrus niloticus*, respectively. The differences between the examined three different fish samples were significant (P<0.01) as shown in table (8). In table (9) ~~and Figure (6),~~ the number of un-accepted samples were 6, 4 and 1 represented as 20% ,13.33% and 3.33% in *Oreochromis niloticus*, *Clarias lazera* and *Mormyrus niloticus*, respectively. So, the all examined samples of fish based on their levels of TMA were acceptable according to EOSQ (2005)

Table 1 Analytical results of pH values in the examined samples of Nile fish

Nile fishes	Min	Max	Mean ± S.E*
Oreochromis niloticus	6.17	6.59	6.36 ± 0.05
Clarias lazera	6.08	6.51	6.19 ± 0.03
Mormyrus niloticus	5.94	6.33	6.07 ± 0.02

S.E* = standard error of mean

Table 2 Analysis of variance (ANOVA) of pH in the examined Nile fish samples.

Source of variance	D.F	S.S	M.S	F. value
Total	89	0.5317		
Between Species (S)	2	0.0356	0.0178	3.12 +
Error	87	0.4961	0.0057	

D.F = Degrees of freedom. S.S = Sum squares. M.S = Mean squares. + = Significant differences (P<0.05)

Table 3 Edibility of the examined samples of Nile fishes based on their pH values (n=30).

Nile fishes	Limit	Accepted samples		Unaccepted samples	
		No.	%	No.	%
Oreochromis niloticus	6.5	27	90	3	10
Clarias lazera	6.5	29	96.67	1	3.33
Mormyrus niloticus	6.5	30	100	0	0
Total (90)		86	95.56	4	4.44

* Egyptian Organization for Standardization and Quality "EOSQ" (2005).

Table 4 Analytical results of Total Volatile Nitrogen "TVN" (mg %) values in the examined samples of Nile fishes

Nile fishes	Min	Max	Mean ± S.E*
Oreochromis niloticus	9.23	35.68	21.58 ± 0.49
Clarias lazera	5.56	29.10	16.73 ± 0.41
Mormyrus niloticus	4.92	26.47	14.15 ± 0.28

S.E* = Standard error of mean

Table 5 Analysis of variance (ANOVA) of TVN in the examined Nile fish samples

Source of variance	D.F	S.S	M.S	F. value
Total	89	74.0157		
Between Species (S)	2	9.4792	4.7396	6.39 ++
Error	87	64.5365	0.7418	

D.F = Degrees of freedom. S.S = Sum squares. M.S = Mean squares. ++ = High significant differences (P<0.01)

Table 6 Edibility of the examined samples of Nile fishes based on their TVN values

Nile fishes	Limit (mg %)*	Accepted samples		Unaccepted samples	
		No.	%	No.	%
Oreochromis niloticus	25	25	83.33	5	16.67
Clarias lazera	25	28	93.33	2	6.67
Mormyrus niloticus	25	29	96.67	1	3.33
Total (90)		83	92.22	7	7.78

* Egyptian Organization for Standardization and Quality "EOSQ" (2005).

Table 7 Analytical results of Trimethylamine "TMA" (mg %) values in the examined samples of Nile fishes (n=30).

Nile fishes	Min	Max	Mean ± S.E*
Oreochromis niloticus	5.16	14.71	8.85 ± 0.22
Clarias lazera	3.84	11.02	6.61 ± 0.15
Mormyrus niloticus	3.19	10.35	5.97 ± 0.13

S.E* = Standard error of mean

Table 8 Analysis of variance (ANOVA) of TMA in the examined Nile fish samples.

Source of variance	D.F	S.S	M.S	F. value
Total	89	41.3895		
Between Species (S)	2	4.9194	2.9597	7.06 ++
Error	87	36.4701	0.4192	

D.F = Degrees of freedom. S.S = Sum squares. M.S = Mean squares. ++ = High significant differences (P<0.01)

Table 9 Edibility of the examined samples of Nile fishes based on their TMA values (n=30).

Nile fishes	Limit (mg %)*	Accepted samples		Unaccepted samples	
		No.	%	No.	%
Oreochromis niloticus	10	24	80	6	20
Clarias lazera	10	26	86.67	4	13.33
Mormyrus niloticus	10	29	96.67	1	3.33
Total (90)		79	87.78	11	12.22

* Egyptian Organization for Standardization and Quality "EOSQ" (2005).

4. DISCUSSION

Regarding the pH value, the current results came in accordance with those reported by Mahmoud (1990), El-Sayed (1991) and Kyrana *et al.* (2002), but lower than those obtained by Sathivel (2005). pH is considered as a limited factor for survival of bacteria in fish (Wipple and Rohvec ,1994) and it decreases uniformly during the frozen storage (Abdullah and Yu 1985). pH value is not a suitable index for freshness assessment, and it can be useful as a guideline for quality control of fish (Ruiz Capillas and Moral, 2001).

Regarding the TVN value, the result were balanced with former studies (El-Marrakchi *et al.*, 1990; Etienne *et al*., 2005), but it was lower than those obtained by Malle *et al. (*1983), who found TVN 18-20 mg/100gm in mackerel*;* Mahmoud ,1990 and Perez-Villarreal and Pozo,1990).???? TVN levels are affected by the method of catch; post-mortem treatment and storage temperature (Olafsdottir *et al*., 1997), also it differs according to species (Nazemroaya *et al*., 2011). TVN is a poor indicator of fish freshness, but it has been used to evaluate fish muscle spoilage (Mazorra-Manzano *et al.,* 2000), and TVN do not reflect the mode of spoilage (Etienne *et al*., 2005). TVN is one of most widely used parameter to evaluate fish quality (El-Marrakchi *et al.,* 1990). TVN levels less than 20mg% indicate fish of good quality; while doubtfully accepted fish contain TVN around 30 mg%, However fish contain 40 mg% consider un-fit for human consumption (Pearson,1984). Oka *et al.* (1989) recorded that initial signs of spoilage appear at 20-25mg% TVN.

Regarding the TMA value, the results obtained were nearly similar to that obtained by Mahmoud (1990), but it was lower than that obtained by Oehlenschlager (1996), Kelly and Yancey, (1999) and Etienne *et al. (*2005). TMA differs according to species (Huss, 1995), also it is affected by storage time and catching season at room temperature or chilling shelves (Hassan, 1995). TMA has been described by Baixas-Nogueras *et al.* (2002) as a good index of quality for many fish species.

The main disadvantage of TMA analysis is it does not reflect the earlier stage of spoilage and is only reliable in certain fish species (Oehlenschlager, 1997). Oka *et al*. (1989) showed that the initial signs of fish spoilage appeared at level of 10-15 mg% TMA.

5. CONCULOSION

This study concluded that the efficiency of application of certain chemical tests for evaluation of fish quality. In this respect, TVN, TMA appeared as reliable indicators for determination of proteolytic activity. *Mormyrus niloticus* is the lowest fish samples in PH, TVN and TMA and this indicated the longer period for availability. *Oreochromis niloticus* should be consumed with caution due to high levels of PH, TVN and TMA which give indication of rapid spoilage.

From this study we recommend that

1. Use of chemical assessment of fish quality as it is rapid accurate method and gives good indication of fish quality.
2. pH is poor indicator of fish quality as it has a wide range of variation among fish species.
3. TVN and TMA are suitable indices of freshness assessment for proteolytic activity.
4. When purchasing fresh whole fish, examine eyes that are clear and bulge slightly. The flesh of whole fish and fillets is firm and shiny. The gills of fresh whole fish are bright red or pink and free of bad slime. The skin is shiny with scales that adhere tightly.
5. There is no discoloration or darkening around the edges of the fish, including the gills. The fish smells fresh, not sour, fishy, or ammonia-like.

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