

# Damanhour Journal of Veterinary Sciences

Journal homepage: https://djvs.journals.ekb.eg/



# **Evaluation of Freshness of Some Imported Marine Fish Species Retailed for Sale in Al Beida City, Libya**

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#### ABSTRACT

A total of 100 random samples of marine water fish represented by Barboni, Morgan, Mackerel and Balameta (25 of each) were collected from local markets at Al Beida City, Libya. Samples were evaluated for their freshness through determination of proteolytic and lipolytic indices. The obtained results revealed that mean values of pH were 6.11 $\pm$ 0.05, 6.17  $\pm$ 0.03, 6.15  $\pm$  0.04 and 6.25  $\pm$ 0.7 for Barboni, Morgan, Mackerel and Balameta, respectively. Also, it was found that the mean of TVN values was  $22.29 \pm 0.26$ ,  $23.27 \pm 0.24$ ,  $27.38 \pm 0.33$  and  $24.19 \pm 0.23$  for Barboni, Morgan, Mackerel and Balameta fish samples, respectively. Also, Trimethylamine (TMA) as proteolytic index of spoilage was determined and it was found that the mean of TMA values was 5.22  $\pm$  0.23, 4.18  $\pm$  $0.18,\,3.32\pm0.33$  and  $4.90\pm0.49$  mg %for Barboni, Morgan, Mackerel and Balameta fish samples, respectively. In addition, Thiobarbituric Acid (TBA) as lipolytic index of spoilage was estimated and it was recorded that the mean of TBA values was 3.9 $\pm$  0.13, 3.6  $\pm$  0.12, 3.8  $\pm$  0.14 and 4.1 ±0.11 mg % for Barboni, Morgan, Mackerel and Balameta fish samples, respectively. Finally, it was found that the mean of peroxide values was  $0.47 \pm 0.06$ ,  $0.41 \pm 0.05$ ,  $0.43 \pm 0.04$ ,  $0.48 \pm 0.06$  med O2/kg for Barboni, Morgan, Mackerel and Balameta fish samples, respectively. Luckily, it was noticed that all of the examined samples of fish are accepted according to permissible limits stipulated by Egyptian Organization for Standardization,

Keywords: Spoilage, Markers, Imported, Marine, Fish

#### 1. Introduction

Fish is a great source of protein, vitamins, minerals, omega-3 fatty acids and a key nutrient for brain development. A well-balanced diet that includes a variety of fish and shellfish can contribute to heart health and children's proper growth and development (Jaclyn et al., 2010). Fish, being one of the exceptionally perishable foods and as a result of globalization of food trade fish products tend to be more susceptible to rejection due to poor quality especially if the initial raw materials are of poor quality despite the technological developments in fish production (FAO, 2009). The quality of fish and fishery products constitute a major concern in fish industry all over the world (Huss et al., 2004). The shelf life of fish could be detected by several methods on of them and most accurate is determining biogenic amines concentration (El-Sayed, 2014). Freezing preserves the taste, texture, and nutritional value of foods better than any other methods and as a result extensive quantities of food are now frozen worldwide (George, 1997).

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P ISSN: 2636-3003 EISSN: 2636-2996

Received: April 13, 2020; Received in revised form: April 19, 2020;

accepted: April 20, 2020.

Sensory assessment has always played a key role in quality and freshness evaluation in the fish industry .The various sensory characteristics, such as outer appearance, odor and color are still very important in the quality systems in the fish processing industry .Sensory inspection of processed fish is used in the fish industry to find defects that have occurred during handling and processing (Oehlenschlanger, 1998).

Freshness assurance is one of the most important goals for the fish industry as freshness is closely related to quality. Sensory, chemical / biochemical and microbiological methods are conventionally used to measure the degree of fish freshness. Texture and color analysis as well as determination of post-mortem pH also provide indications of physical changes occurring in fish muscle during storage (Izumi, 2012).

Volatile amines (TVN, Trimethyl- amine) are the characteristic molecules responsible for the fishy odor and flavor present in fish several days after the catch and they are commonly used as criteria for assessing the fish quality (Etienne, 2005).

The present study was carried out for assessment of quality indices of four species of marine fish including; Barboni, Morgan, Mackerel and Balameta through determination of pH, Total Volatile Nitrogen (TVN), Trimethyl amine (TMA), Thiobarbituric acid (TBA), Peroxide value (PV) and Free Fatty acids (FFA).

## 2. Material and methods

#### 2.1. Collection of samples:

A total of 100 random samples of marine water fish represented by Barboni, Morgan, Mackerel and Balameta (25 of each) were collected from local markets at Al Beida City, Libya. Samples were collected in semi chilled state and moderate weight and kept in a separate sterile plastic bag and transferred in an ice box as soon as to the laboratory of the Food Hygiene Department, Faculty of Veterinary Medicine, Alexandria University under possible aseptic conditions.

- 2.2. Chemical evaluation of fish samples:
- 2.2.1. Determination of pH (Pearson, 2006).
- 2.2.2. Determination of Total volatile Nitrogen (TVN) (FAO, 1980).
- 2.2.3. Determination of Trimethylamine (TMA) (FAO, 1980).
- 2.2.4. Determination of Thiobarbituric Acid Number (TBA) (Pikul et al., 1989).
- 2.2.5. Determination of Peroxide value (PV) (Asakawa and Matsushita, 1978).
- 2.2.6. Determination of Free Fatty Acids (FFA) (Folch et al., 1957).
- 2.3. Statistical Analysis:

The obtained results were statistically evaluated by application of Analysis of Variance (ANOVA) test according to Feldman et al. (2003).

## 3. Results and Discussion

#### 4.1. Determination of pH value:

The measurement of pH value is described as a simple method for detecting imported frozen fish quality. Where pH value is among the most critical factors affecting microbial growth and spoilage of foods in general. The pH value was an indication of the extent of microbial spoilage in fish (Eyo, 2001). Data in Table (1) declared that mean values of pH values of the examined fish samples were  $6.11\pm0.05$ ,  $6.17\pm0.03$ ,  $6.15\pm0.04$  and  $6.25\pm0.7$  for Barboni, Morgan, Mackerel and Balameta, respectively. In addition, it was noticed that the highest mean of pH values was determined in samples of Balameta fish followed by Morgan fish then Mackerel and lastly Barboni. Moreover, it was noticed that all of the examined samples were within the permissible limit (6.5) recommended

by EOS, (2005). The current results come in accordance with those reported by Mahmoud (1990); El-Sayed (1991) and Kyrana et al. (2002) and lower than those obtained by Sathivel, (2005). pH value is not suitable index for freshness assessment and it can be useful as a guideline for quality control of fish (Ruiz-Capillas and Moral, 2001).

#### 4.2. Determination of Total volatile nitrogen (TVN):

TVB-N 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 and they don't reflect the mode of spoilage, bacterial or autolytic (Baixas-Nogueras et al., 2002). TVN is one of most widely used parameter to evaluate fish quality (El-Marrakchi et al., 1990). It is evident from results recorded in Table (2) that the mean of TVN values for examined fish samples was 22.29  $\pm$  0.26, 23.27  $\pm$  0.24, 27.38  $\pm$  0.33 and 24.19 ±0.23 for Barboni, Morgan, Mackerel and Balameta fish samples, respectively. In addition, it was noticed that the highest mean of TVN values was determined in samples of Mackerel fish followed by Balameta, Morgan and lastly Barboni. Moreover, it was noticed that all of the examined samples were within the permissible limit (30 mg %) recommended by EOS, (2005). The result were balanced with those of El-Marrakchi et al., (1990) and Etienne, (2005), while lower than Malle et al., (1983) who found TVN 18-20 mg/100gm in Mackerel. TVN levels are affected by the method of catch; post mortem treatment and storage temperature (Olafsdottir et al., 1997), also differ according to species (Nazemroaya et al., 2011). TVN levels less than 20 mg % 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). The fish treatments such as chilling, ice storage, slurry ice, freezing, cooking, canning, packaging, modified atmosphere influence the volatile amine content (Etienne, 2005).

#### 4.3. Determination of Trimethylamine:

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). As shown in Table (3), it was found that the mean of TMA values for examined fish samples was 5.22  $\pm$  0.23, 4.18  $\pm$  0.18, 3.32  $\pm$  0.33 and 4.90  $\pm$ 0.49 for Barboni, Morgan, Mackerel and Balameta fish samples, respectively. In addition, it was noticed that the highest mean of TMA values was determined in samples of Barboni fish followed by Balameta, Morgan and lastly Mackerel. Moreover, it was noticed that all of the examined samples were within the permissible limit (10 mg %) recommended by EOS, (2005). The result obtained were nearly similar to that obtained by Mahmoud, (1990) and lower than that obtained by Oehlenschlager, (1996); Kelly and Yancey, (1999) and Etienne, (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).

### 4.4. Determination of Thiobarbituric acid:

TBA is a widely used as indicator for the assessment of degree of secondary lipid oxidation (Ozyurt et al., 2007). TBA is an important quality index for fatty fish (Lynch and Frei, 1993). Results achieved in Table (4) revealed that the mean of TBA values for examined fish samples was  $3.9\pm0.13$ ,  $3.6\pm0.12$ ,  $3.8\pm0.14$  and  $4.1\pm0.11$  for Barboni, Morgan, Mackerel and Balameta fish samples, respectively. Also, it was noticed that the highest mean of TMA values was determined in samples of Mackerel fish followed by Balameta, Barboni and lastly Morgan. Moreover, it was noticed that all of the examined samples were within the permissible limit (4.5 mg %) recommended by EOS, (2005). The results were higher than those obtained by Gülsün et al., (2009) and Nazemroaya et al., (2011), While lower than that obtained by Vafakhah et al., (2014). Generally, TBA values agree with the fact that the higher lipid contents, the higher TBA value in fish (Caponia et al., 2004).

## 4.5. Determination of peroxide value:

Peroxide value is widely used as an indicator for the assessment of degree of primary lipid oxidation (Masoud et al., 2008) and oxidative rancidity (Vafakhah et al., 2014). Data tabulated in Table (5) showed that the mean of peroxide values for examined fish samples was  $0.47 \pm 0.06$ ,  $0.41 \pm 0.05$ ,  $0.43 \pm 0.04$ ,  $0.48 \pm 0.06$  meq O2/kg for Barboni, Morgan, Mackerel and Balameta fish samples, respectively. Also, it was noticed that the highest mean of PV values was determined in samples of Balameta fish followed by Barboni, Mackerel and lastly Morgan. The results from current study were lower than those obtained by Gülsün et al., (2009) and

Vafakhah et al., (2014). PV value affect by the time passes from the onset of catching till ice storage as the fish immediately storage after catching show increase in the PV to 8.2 meq/kg fat , but for those of delayed iced storage about 10 h PV value increased to 24.60 meq/kg of fat (Connell, 1995).

#### 4.6. Determination of Free fatty acids:

Fat spoilage is considered the most important factor that lower fish quality (Connell, 2002) as it produces undesirable taste (Balachandran, 2001), color as well as alters nutritional value of fish (Clark et al., 1997). Moreover, FFA changes were used as indicator of hydrolytic rancidity (Vafakhah et al., 2014). Free fatty acids (FFA) as lipolytic index of spoilage were estimated for fish samples. As shown in Table (6), it was found that the mean values of FFA for the examined fish samples was  $0.28 \pm 0.03$ ,  $0.26 \pm 0.02$ ,  $0.31 \pm 0.04$  and  $0.29 \pm 0.05$  for Barboni, Morgan, Mackerel and Balameta fish samples, respectively. Also, it was noticed that the highest mean of PV values was determined in samples of Mackerel fish followed by Balameta, Barboni and lastly Morgan. The results were lower than those obtained by Gülsün et al., (2009), Nazemroaya et al., (2011) and Vafakhah et al., (2014). Free fatty acids formation during ice storage (hydrolytic rancidity) is due to the presence of poly unsaturated FA leading to negative sensory impact related to FFAs (Bremner, 2002). They have shown to undergo faster oxidation rate than bigger lipid classes of triglycerides and phospholipids which affect the dietary quality of fish (Losada et al., 2007).

#### 4. Conclusion

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; however, TBA is a good index for demonstration of fat rancidity as well as PV as an indicator for assessment of primary lipid oxidation. In addition, it was found that Barboni and Mackerel should be consumed with caution due to high levels of TVN, TMA, TBA and PV which give indication of rapid spoilage as well as high levels of histamine. Also, Morgan is the lowest fish samples in TVN, TMA, TBA and PV and this indicated the longer period for availability.

#### Conflict of interest statement

No conflicts of interest.

#### Funding

The authors declared that they received no financial support for their research and/or authorship of this article.

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Table (1): Statistical analytical results of pH values of fish samples (n=25/each)

Fish species	Min.	Max.	Mean $\pm$ S.E*
Barboni	5.9	6.39	$6.11 \pm 0.05$
Morgan	6.1	6.31	$6.17 \pm 0.03$
Mackerel	6.2	6.34	$6.15 \pm 0.04$
Balameta	6.12	6.29	6.25 ±0.7

Permissible limits of pH should not exceed 6.5 according to Egyptian Organization for Standardization (EOS), (2005).

 $S.E^* = standard error of mean$ 

Table (2): Statistical analytical results of Total Volatile Nitrogen (TVN) (mg %) as proteolytic index of spoilage of fish samples (n=25/each)

Fish species	Min.	Max.	Mean ± S.E*
Barboni	16.13	28.49	$22.29 \pm 0.26$
Morgan	19.19	26.41	$23.27 \pm 0.24$
Mackerel	21.95	29.28	$27.38 \pm 0.33$
Balameta	22.62	28.18	24.19 ±0.23

Permissible limits of TVN should not exceed 30 mg % according to EOS, (2005). It was found that all of the examined samples of fish are accepted based on their levels of TVN according to permissible limit stipulated by EOS, (2005).

Table (3): Statistical analytical results of trimethylamine (TMA) (mg %) as proteolytic index of spoilage of fish samples (n=25/each)

Fish species	Min.	Max.	Mean $\pm$ S.E*
Barboni	3.62	8.16	$5.22 \pm 0.23$
Morgan	3.21	6.24	$4.18 \pm 0.18$
Mackerel	2.39	7.18	$3.32 \pm 0.33$
Balameta	3.24	5.90	$4.90 \pm 0.49$

Permissible limits of TMA should not exceed 10 mg % according to EOS, (2005). It was found that all of the examined samples of fish are accepted based on their levels of TMA according to permissible limit stipulated by EOS, (2005).

Table (4): Statistical analytical results of thiobarbituric acid (TBA) (mg %) as lipolytic index of spoilage of the examined fish samples (n=25/each)

Fish species	Min.	Max.	Mean ± S.E*
Barboni	3.1	4.2	$3.9\pm0.13$
Morgan	2.7	4.1	$3.6 \pm 0.12$
Mackerel	3.2	4.3	$3.8 \pm 0.14$
Balameta	3.3	4.4	4.1 +0.11

Permissible limits of TMA should not exceed 4.5 mg % according to EOS, (2005). It was found that all of the examined samples of fish are accepted based on their levels of TBA according to permissible limit stipulated by EOS, (2005).

Table (5): Statistical analytical results of peroxide value (mg/kg) as lipolytic index of spoilage of the examined fish samples (n=25)

Fish species	Min.	Max.	Mean ± S.E*
Barboni	0.34	0.58	$0.47 \pm 0.06$
Morgan	0.29	0.49	$0.41 \pm 0.05$
Mackerel	0.31	0.51	$0.43 \pm 0.04$
Balameta	0.36	0.53	0.48 ±0.06

Table (6): Statistical analytical results of free fatty acids (mg %) in the examined fish samples (n=25)

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Fish species	Min.	Max.	Mean ± S.E*
Barboni	0.19	0.42	$0.28 \pm 0.03$
Morgan	0.15	0.38	$0.26 \pm 0.02$
Mackerel	0.17	0.44	$0.31 \pm 0.04$
Balameta	0.16	0.40	0.29 +0.05