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Physicochemical Indicators of Spoilage in Marinated Fish Products: A Review

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Abstract

Marinated fish products are semi-preserved foods that have gained popularity worldwide due to their extended shelf life and enhanced nutritional value. Historically, marinating has been a traditional method of preserving fish, involving vinegar, salt, and spices. This review focuses on the physicochemical indicators of spoilage in marinated fish products, including changes in sensory characteristics, pH, and lipid oxidation. Recent studies have shown that these indicators are critical for predicting marinated fish shelf life and quality. Advanced technologies, such as vacuum tumbling and cold marinating, have also been explored to improve these products' preservation and sensory characteristics. Understanding and monitoring these physicochemical indicators are essential for ensuring the safety and quality of marinated fish products, eventually contributing to food security and consumer health.

Keywords: Fish product, marinating, physicochemical changes, spoilage

Introduction

Historical Background in Marinating Fishery Products

Marinated fish are semi-preserved fishery products that are popular in many countries (Capaccioni, Casales, & Yeannes, 2011). Fatty fish such as herring, sardine, mackerel, and anchovies, as well as other crustaceans and bivalves, are the usual subject for marinating (Arason et al., 2014). Historically, marinating of fish began in 1300's during the Renaissance period. It was spread worldwide during French and Spanish colonization and was further improved specifically in Asian countries by applying different methods and ingredients or additives to satisfy their taste (Yuan et al., 2022).

Traditionally, marinating involves soaking fish in a marinade solution that has already been prepared with the most common ingredients such as vinegar, salt, sugar, spices, oil, and acids from citrus fruits (Arason et al., 2014). During the Porcelain period, Philippine ancestors often used marinating as a way of fermenting fish as introduced by Spanish colonizers, they also consider this method as the first step in doing other fish processing methods like sun drying wherein vinegar and brine are the most used solution (Shenderyuk & Bykowski, 2020). The most common marinated fishery products in the country are anchovies, marinated mussels, and marinated sardines or mackerel (Tahiluddin & Kadak, 2022). Nowadays, with the presence of technology and advancements in preparing and preservation of fish products, new ways of marinating fish and other meat products have been introduced mostly in the processing industry such as cold marinating, cook marinating, fried marinating, and pasteurized marinating (Capaccioni et al., 2011).

This review aims to provide an overview of the physicochemical indicators of spoilage in marinated fish products, discuss the mechanisms underlying these indicators, and explore recent technological advancements in marinating techniques. In understanding and monitoring these indicators, the food industry can better ensure the quality and safety of marinated fish products, eventually contributing to consumer health and food security.

Importance of Marinating Fish and its Consumption Benefits

Marinating as a way of processing fish that promotes food security and value-adding purpose. This method of preserving fish not just extends the shelf life, but also provides enhanced nutritional value and flavor of processed fish (Bell et al., 2009). According to Sampels (2015), the marinating procedure applied to any fish products is of great help in the reduction of the spoilage rate of fish. In addition to that, the later also stated how this processing technique can boost the nutritional value of the fish if they are implemented properly and in an innovative way. Accordingly, one of the common ways of marinating fish is through vinegar which lowers the pH and lowers the percentage of bacterial growth of the fish. Other than that, Pedro and Nunes (2019), also stated that brining is also a type of marinating fish. In their study, it is stated how the brining of fish is commonly used for the preservation processes as they describe how fungi, bacteria, and other living pathogenic organisms die due to the high levels of salt concentration. During the marinating trials conducted by Jääskeläinen et al. (2023), it was found that the fish they used had a longer shelf life. Using different salt-based marinades, they were able to prolong the shelf of their fish. In addition, Babikova et al., (2020), also stated that the marinating process also increased ash content and reduced the water content of the fish they used during their experiment. The results showed how marinating improved the preservation of the fish and increased the salt content thereby preventing microbial growth.

Aside from preservation, marinating is also proven effective in maintaining the nutritional value of the fish. Çorapci et al. (2020) through their 180-day experiment and investigation on sea bream (*Sparus aurata* L., 1758), found that the application of several spices and oils not only preserved the nutritional value but also helped in maintaining the fatty acids of the fish which is essential for maintaining a healthy heart as it reduces the cholesterol level. Arason et al. (2014) stated that marinating also includes massaging the muscles of the fish to incorporate the spices. Thus, this will make the muscles swell due to the protein and the other nutrients coming inside the fish. In this way, the nutritional level of the fish will elevate as it absorbs more of the spices.

In addition, marinating fish and consuming marinated fish products is beneficial to the diet because they include amino acids such as aspartic acid, glutamic acid, and lysine, which account for around 31% of total amino acids. Many amino acids, including alanine and glycine contribute to the final flavor and taste of the marinated product (Behera et al.2020).

Current Status of Aquatic Post-Harvest and Fish Marinating in the Philippines

As an archipelagic state, the Philippines is known for abundant fisheries and aquatic resources. The fishing industry makes a substantial contribution to the national economy by creating direct revenue and job opportunities (Yap et al., 2016). In 2022, the fisheries production recorded a total volume of 4.34 million MT, and a value of PhP 326.57 billion (BFAR, 2023). Fish and fishery products are the second most consumed food items in the Philippines, following rice and rice products. They make up 11.70% of the daily intake of each Filipino, totalling to 93.90% grams per day. This is 63.00% higher than meat and meat products, and 206.00% higher than poultr (BFAR, 2023). According to survey report, each Filipino consumes an average of 34.27 kg/year of fish and fishery products comprising of 23.36 kg of fresh fish, 2.85 kg of dried fish (as fresh fish), 4.97 kg of processed fish, and 3.10 kg of crustaceans and mollusks (BFAR, 2023). The Philippines is known to produce smoked, dried, canned, and salted fishery products (Garcia, Mohan Dey, & Navarez 2005; Cain, 2019). The traditional fish processing technique is highly used in the Philippines, but it was later expanded into modern fish processing with the help of technology and done commercially to supply massive amounts of processed fish products across the country and for export purposes (Tahiluddin & Kadak, 2022).

In terms of international trade, the fishery industry registered a net surplus of USD 292.25 million from the total export value of USD 1.21 billion and import value of USD 920.46 million in 2022 (BFAR, 2023). In 2022, the country's volume of exported fish and fishery/aquatic products registered 282,674 MT and has a corresponding value of PhP 66.07 billion. The majority or 79.14% of the exported commodities were classified as fish, crustaceans, molluscs, and other prepared or preserved products. In totality, these commodities posted 223,703 MT of export volume with a value amounting to PhP 46.26 billion. Meanwhile, the remaining commodities were shells, miscellaneous fishery products and other derivatives (BFAR, 2023). Among these products are marinated products of different fish species. Marinating as one of the most common fish processing techniques in the country adds options on how we should serve our fish dish for our day to day meals (Arason et al., 2014). The Philippines usually practice the common way of marinating fish using vinegar, salt, spices, and sugar.

They often use anchovies, mussels, sardines, and mackerel as raw materials for marinating (Shenderyuk & Bykowski, 2020).

Factors Influencing the Spoilage of Marinated Fish Raw materials

Despite the preservative effects of marinating, spoilage can still occur in marinated fish products due to several factors. The quality of the raw fish used in marinating significantly influences the shelf life of the finished product. The chemical composition of fish, particularly its lipid content, varies depending on the species and handling procedures before marinating (Sorio & Inolino, 2018). Fatty fish, such as herring and mackerel, have a higher spoilage rate compared to lean fish due to their higher lipid content, which is more susceptible to oxidation (Zugarramurdi et al., 2004). This oxidation can lead to rancidity and off-flavors, affecting the quality and safety of the product.

Spoilage in marinated fish compromises the product's quality and poses significant risks to food safety. Spoiled fish can harbor harmful pathogens, leading to foodborne illnesses if consumed (Gamage et al., 2017). For instance, improper handling and storage conditions can facilitate the growth of bacteria like *Clostridium botulinum* and *Staphylococcus aureus*, which can produce toxins harmful to human health (Sampels, 2015). Identifying reliable physicochemical indicators of spoilage is important for ensuring the safety and quality of marinated fish products. These indicators, such as changes in pH, water content, and lipid oxidation levels, can provide early warnings of spoilage, allowing for timely interventions to prevent further deterioration (Pons-Sánchez-Cascado et al., 2005).

The use of proper handling and storage conditions, such as chilling, is essential to inhibit enzymatic activity and prevent lipid oxidation, thereby maintaining the initial quality of the fish (Gamage et al., 2017). Additionally, the composition of the marinade itself can influence spoilage by affecting the pH and water activity of the fish, which in turn impacts microbial growth (Shenderyuk & Bykowski, 2020). For example, marinades containing citric acid can enhance antimicrobial properties and extend shelf life by inhibiting spoilage bacteria (Bou et al., 2017). Understanding these factors and monitoring physicochemical indicators are necessary for maintaining the quality and safety of marinated fish products.

Methods of Marinating

The method or procedure applied in marinating any types of fish has a great influence on its physicochemical characteristics and shelf life (Gupta, Gandotra et al., 2015). A conventional method of marinating fish through immersion only lasts for 3-5 days when stored at room temperature, and this may extend for months if chilled or stored at a low temperature depending on the ingredients used (Gamage et al., 2017). Degebassa and Tigabu (2009) evaluate the chemical properties and shelf life of cold, cooked, and fried marinated Nile tilapia fillet, wherein all samples were marinated in a mixture of vinegar and salt solution. After 60 days of storage, fried marinated samples exhibit a pleasant odor, and moisture content of 60.77%. They also estimated that the maximum shelf life of fried marinated samples was 6 months compared to 4 months of other samples without facing any problems. This result may be due to frying procedure done prior to marinating process. According to Secci and Parisi (2016), frying absolutely removes water in the fish muscle and thereby inhibits the growth of spoilage bacteria, they also added that high temperature of oil used in frying may prevent oxidative damage and preserving the quality of fish for 3-4 days at a normal room temperature.

Another study conducted by Nino, Sasidharan, et al. (2022), they examined the impact of vacuum tumbling-assisted marinating on the nutritional composition, and sensory acceptability of deep-fried Indian white shrimp (*Penaeus indicus*). The authors used internal vacuum pressure while marinating the shrimp. The result showed more acceptable sensorial characteristics than of the conventional marinating, they also observed that the product recorded a 45% oil uptake after frying, and 90% reduction on the marinating time. Lombard and Lanier (2011) also stated in their study that vacuum tumbling-assisted marinating can establish or produce ready-to-eat (RTE) deep-fried products from Indian white shrimp which is superior to traditional marinating in terms of processing time and oil uptake while uncompromising sensory acceptability. Table 1 shows the different methods of marinating fish and their effect on the final product.

Table 1. Different methods in marinating fish and its effect on the final product

METHOD	DEFINITION	EFFECTS ON THE FINAL PRODUCT	REFERENCE
Immersion	Involves soaking of fish meat in a prepared liquid marinade and allowing the ingredients to penetrate the flesh through diffusion over time.	Enhanced tenderness of the fish flesh. Changes in the color appearance depending on the type of marinade used, and improved flavor.	Van Haute, Raes, Van Der Meeren, & Sampers (2016)
Injection	Marinades are injected into the fish flesh through the use of needles and probes, immediately spreading the marinade into the flesh.	Flavor and ingredients are evenly distributed into the flesh, providing a ready-to-cook fish as it doesn't require an amount of time like immersion.	Çağlak & Karslı (2015)
Tumbling	Usually done in fish processing plants, specifically in a canning procedure where fish are put in a thin can together with a sauce that serves as a marinade.	Provide longer shelf life, ready-to-cook, enhanced juiciness, and value-added fish product.	Nino et al. (2022)
Dry marinating	This involves rubbing dry marinades such as brown sugar, salt, paprika, and cumin. Usually done in fish like tuna, salmon, and trout.	Seals in the moisture in the fish flesh and provide a textured outer layer of the flesh or crust.	Sampels (2015)

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Marinating ingredients and additives

Marinating ingredients has a direct influence on the shelf life and quality of the final product, a typical marinade is composed of three essential components, these include acid like vinegar or citrus, oils like sesame or olive oil, and flavouring agent such as herbs and spices. These components have roles in inhibiting the growth of spoilage bacteria and maintaining the volatile base nitrogen at low levels (Nieminen et al., 2012). Based on the study of Fernandes et al., (2016) marinades containing various combinations of soy sauce, sorbitol, sucrose, and citric acid on blue whiting fish produced adverse effect on the sensory characteristics, and physicochemical profile of the final product.

Their findings revealed that the variety of marinade components and dosages had a specific influence on the sensory characteristics of marinated blue whiting fillets. The sweetness flavor was greatly boosted by sucrose coupled with soy sauce, whereas the sour flavor was significantly enhanced by citric acid. Soy sauce also had a little impact on odor characteristics. The marinated fish had a rubbery texture compared to the untreated samples (Fernandes et al., 2016). They also added that marinade components also had influence on color wherein soy sauce increased the redness of the product, but citric acid diminished the redness. Moreover, citric acid in the marinade solution contributes to the extended shelf life of the blue whiting fish (Fernandes et al., 2016). According to Dogruyol et al., (2020), citric acid is a dicarboxylic acid that enhances antimicrobial power of fish products. With as little as 1% of citric acid, it is enough to kill or inhibit a wide range of spoilage bacteria.

Additives in marinating fish are proven to be good at enhancing flavor, appearance, product yield and also the shelf-life of fish (Gamage et al., 2017). Marinades made from citrus fruits tend to enhance the juiciness and tenderness of the fish because citrus fruits are capable of breaking down the protein in the fish muscle and thereby increasing its water holding capacity (Baygar et al., 2010).

Involvement of additives during marinating process not just enhances the sensory characteristics of the fish, it also improves nutritional value of the finished product especially when fruits and herbs are used (Gokoglu et al., 2017). According to Sen and Temelli (2003), the used of vegetable oil additives and ascorbic acid together with garlic marinade, hot pepper sauce, and green olive oil significantly boost the antimicrobial property of marinated anchovy, and extend its shelf life due to its antioxidant property. Based on their obtained result, the above-mentioned marinades brought no adverse effect on its microbial characteristics, and the marinated anchovy fillets showed no pathogenic microorganism that may potentially harm public health.

According to Rostamzad, et al., (2011), ascorbic acid can be used primarily as antioxidant that can provide nutritional and preservation benefits to any fish products, it also slows the oxidation of fish muscle and thereby preserve its natural color and freshness. Also, the low pH of ascorbic provides inhibitory effects of most spoilage bacteria that delays the spoilage rate of marinated fish products (Sen & Temelli, 2003). Table 2 shows the common ingredients in marinating fish and its function

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Table 2. Different ingredients in marinating fish and its function.

MARINATING INGREDIENTS	FUNCTION	REFERENCE
Vinegar	Changes the texture of the food. Breaks down the chemical structure of protein resulting in a tenderness in the flesh of fish. Also capable of extending shelf life of the product by killing spoilage bacteria.	Pons-Sánchez-Cascado et al. (2005)
Salt	Aids the process of osmosis by removing moisture and juice from the fish flesh and then juice is absorbed back into the flesh together with the flavor from the marinade and provides additional preservation purpose.	Topuz (2016)
Citrus juice	Improve the flavor and sensory characteristics of the product. Also helps the protein in fish flesh retain water, increasing the water holding capacity of the final product. Additionally, citric acid present in citrus extract is great at inhibiting growth of thermophilic bacteria.	Šimat et al. (2019)
Wine	Wine acts as a tenderizer of the crust or surface of the fish flesh when cooking, it also provide added moisture and flavor. Wine also possesses alcohol, acids and tannins that are great in preserving meat or fish products.	Yi, Zhang, Ding, Hu, Liao, & Zhang (2013)
Sunflower oil	Used as an additional ingredient in a marinade that is a great help in infusing flavor of ingredients and acids to the fish flesh.	Kocatepe et al. (2019)
Sesame oil	Sesame oil serves as the flavor enhancer of the marinade. The antioxidant component of sesame oil is a great help in delaying the spoilage of fish.	Kocatepe et al. (2019)
Herbs and spices	The components of herbs and spices like thyme, oregano, basil, sage and rosemary provide added flavor to the final product. These ingredients also contain a variety of antioxidant and antibacterial components that adds preservative value to the fish marinade.	Van Haute et al. (2016)

Temperature and storage condition

Most changes that cause spoilage in fish are affected by temperature. In most fish species, increasing the temperature from 0°C-4°C will double the rate of spoilage and cut the shelf life of the fish into half (Mei, Ma, & Xie, 2019). An ideal storage condition for a processed fish must be in an enclosed space with a temperature below 4°C, fish should be packed tightly in a container, plastic, foil or moisture proof paper (Khalafpour & Roomiani, 2022).

In the study of Szymczak et al., (2020), the marinated Atlantic and Baltic herring fillets were frozen and kept for 2 days – 5 months at constant and fluctuating temperatures that often cause recrystallization. Marinades that have been frozen and thawed increased the firmness, color, and overall sensory properties of the fish. Temperature changes accelerate the degradation of muscle tissue structure and lysosomal membranes, boosting the activity of aspartyl endopeptidase, which improves meat texture and increases the concentration of protein-hydrolyzing of fish (Kocatepe et al., 2019). After 3 months of frozen storage with temperature fluctuations, the largest thaw drip loss and lipid oxidation were found. Frozen storage had a different effect on fatty and thin herrings. While frozen-thawed marinades stored for up to 5 months were of good microbiology quality (Szymczak et al., 2020). Based on the result of the study, it shows that the freezing of the semi-marinades may be one of the methods for quality improvement and for extending marinades shelf-life before the seasonal increase of the said fish species demand on the market.

Other than that, Hematyar et al., (2018) conducted a study to find out the effects of frozen storage on the protein and lipid oxidation, firmness, liquid loss, sensory properties, and nutritional values in marinated common carp fillets during 6 months of frozen storage at a temperature of -20°C. Based on the results obtained, no adverse changes in chemical and sensorial properties were recorded during the storage period. It goes to show that the severe low temperature was able to preserve the quality of marinated fish by completely eliminating water activity (Hematyar et al., 2018).

Physicochemical Properties of Marinated Fish Products that Indicates Spoilage

The physicochemical characteristics include four components, these are the sensory characteristics, pH, Thiobarbituric Acid-Reactive Substance (TBARS), and Total Volatile Base Nitrogen (TVBN). These components are critical in identifying the quality and spoilage of specific fish products. They also possess standard numerical values or limits that are important to determine the degree of acceptability of a certain product except for the sensory characteristics (Essid et al, 2020). Table 3 shows the standard numerical value for the physicochemical parameters of marinated fish.

Table 3. Standard numerical value of pH, Thiobarbituric Acid - Reactive Substance (TBARS), and Total Volatile Base Nitrogen (TVBN)

PHYSICOCHEMICAL PROPERTIES	STANDARD NUMERICAL VALUE	REFERENCE
pH	< 4.8	Essid et al. (2020)
TBARS	< 3 mg MDA/kg	Essid et al. (2020)
TVBN	< 35 mg N/100 g	Kumar & Mathew (2016)

Sensory characteristics

Sensory assessment is described as the scientific discipline of remembering, measuring, analyzing, and interpreting reactions to food features as perceived by the senses of sight, smell, taste, touch, and hearing. It employs psychological strategies to assess the physical attributes of food (Green, 2010). Sensory procedures are used to measure qualities that cannot be directly examined by physical or chemical testing. Conducting sensory tests may not seem difficult in layman's terms but it is not as easy as it seems (Zhou et al., 2016). If sensory testing is not done properly, the data gathered will not show the genuine situation. It is vital to be familiar with these procedures to understand when and how to utilize them, and to have a well screened and trained panel (Hassoun & Karoui, 2017).

In performing sensory evaluation, the following parameters such as appearance, taste, odor, and texture are being assessed to identify if the subject is acceptable or not (Zhou et al., 2016). Food appreciation and choices are often influenced by quality aspects related to appearance. Color and appearance play a vital role in the selection and acceptance of processed fish products. The appearance of marinated fish may vary depending on the ingredients used (Abraha et al., 2018). A newly marinated fish must be sleek in color due to the acid component; dull color of fish muscle indicates long period of exposure to marinade (Hassoun & Karoui, 2017). Taste is a chemical sense that serves as both a warning and a feeding mechanism, and only soluble compounds can cause flavor. Salivary glands are vital in tasting because they dissolve tasteful substances and transport them to taste receptors (Xue, et al., 2021).

Odor is defined as anything that can be smelled. It is the quality of a food that is felt by inhalation in the nasal or oral cavities. Odor stimuli affect only a small area of the receptor cells located in the ceiling of the inner nose. Odorless would be the verdict when such a sensory stimulus is not received (Gao et al.,

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2020). The sense of touch is addressed by texture.

Texture includes any feeling that affects the skin or muscle endings. The basis in conducting textue assessment of processed food included finger and mouth feel. It is also suggested that such attributes of mouth feel as chewiness, fibrousness, grittiness, mealiness, stickiness, oiliness are essentially sensed by the muscular force applied in the process of mastication are considered part of texture (Chandra & Shamasundar, 2015). Objective measurements of texture can be done using a texturometer. A texturometer may be used to take objective texture measurements. The basic texturometer system consists of a plunger that compresses the sample at a constant rate, with the forces created being monitored by a strain gauge (Bernardo et al., 2022).

In doing the sensory evaluation, there are different methods and each of them are differ based on their setup and subsequent statistical analysis (Zhou et al., 2016). Table 4 shows the different methods used in evaluating sensory characteristics of processed fish.

Table 4. Methods in evaluating sensory properties of marinated fish and their basic setup (Velickova, 2017).

SENSORY EVALUATION METHOD	QUESTION TO BE ASKED	BASIC SETUP
Discrimination or difference test	Are products different?	20-50 panelists
	Which sample has a greater intensity of an attribute?	Screened for acuity (keenness or sharpness of perception, *i.e.* can they smell and taste well?). Done through a series of sensorial test
Descriptive analysis	If products are different, how are they different?	8-12 panelists or 6 -10 panelists.
	What is the magnitude of these differences?	Panelists are asked to rate intensity for all sensory attributes.
Affective or preference, and hedonic test	What is the acceptability of a product? Is the product liked? Is one product preferred over another?	75-150 panelists per test
		Asked degree of liking (how much do they like it) and preference questions.

In the study of Adeyemi et al. (2013), they investigated the changes in the sensory characteristics of African catfish marinated in moringa marinade using the 9-point hedonic scale. The 9-point Hedonic scale is the most commonly used scale to measure someone's degree of liking. In 1949, it was first introduced as a menu planner for American soldiers and has been consistently used in both academic and industrial consumer research all throughout the world. It comprises nine categories ranging from "like extremely" to "dislike extremely" (Kozak & Cliff, 2013). The subsequent statistical analysis of the 9-point hedonic scale is done by giving numerical value to each category with 9 for "like extremely" as the highest and 1 for "dislike extremely" as the lowest (Feng & O'Mahony, 2017). The result in the investigation of Adeyemi et al. (2013) shows that all marinated samples exhibit dark coloration due to the extract that the moringa leaves excretes. Thus, decreasing scores in the appearance of the marinated samples were recorded during the storage period. As to the

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taste and texture, marinated samples received acceptable feedback after storage. Other than that, Trabelsi et al. (2021) conducted a study on the effect of flavored olive oil on marinated anchovy, and one of the parameters that the authors assessed was the sensory characteristics, specifically the taste wherein they utilized the e-sensing analysis using electronic tongue.

Electronic tongue refers to any electrochemical nonspecific multisensory system with global selectivity that aims to emulate the taste capabilities of the human tongue (Mabuchi, Ishimaru, Tanaka, Kawaguchi, & Tanimoto, 2018). Electronic tongues have been used extensively and successfully as taste sensors in the food and pharmaceutical industries, and they offer a lot of potential as an additional analytical tool for regular sensory examination. Electronic tongues are mostly employed to provide qualitative information about the sample under study, with just a few exceptions where they are also used to forecast the concentration of species in the sample (Aouadi et al., 2020). The fundamental idea behind an electronic tongue is to use pattern recognition algorithms to examine the information received from a variety of overlapping, non-specific sensors (Mabuchi et al., 2018). This technology aims to provide fast, accurate, bioinspired potentiometric, voltammetric, and amperometry green sensor-based tools in evaluating processed food products (Di Rosa, Leone, Cheli, & Chiofalo, 2017).

The result of the study conducted by Trabelsi et al. (2021) shows that the marinated samples exhibited good acceptability. The odor and color obtained a decreasing score all throughout the storage period. As to the taste, the authors mentioned that storage does not affect the scores obtained from the said parameter. They also added that the use of e-sensing technology shows great potential in the fish processing industry. Table 5 shows the summary of studies conducted that identify the sensory characteristics of fish using different marinades.

Table 5. Summary of studies that identified the sensory characteristics of fish using different marinades.

FISH	MARINADE USED	EFFECTS ON SENSORY CHARACTERISTICS OF THE PRODUCT	REFERENCE
African catfish	Moringa marinade	The moringa extract present in the marinade causes dark coloration that intensifies as the storage time increases. However, taste and texture are acceptable to the panellists.	Adeyemi et al. (2013)
Anchovy	Marinade with flavored olive oil	Odor and texture of the product are significantly changing in an unappealing form as the storage time increases. However, the texture improved, achieving tenderness after storage.	Trabelsi et al. (2021)

pH

The pH of a marinated fish is a direct result of the amount of free hydrogen ions present in the fish product. These hydrogen ions are released by acids in fish muscle, giving a unique sour flavor (Abdollahi et al., 2020). pH may be thought of as a measure of free acidity, and it is defined more accurately as the negative log of hydrogen ion concentration. If a food has a pH of 3.0, the concentration of hydrogen ions in that food is 10^{-3} moles/L. If the pH is 6.0, the concentration of hydrogen ions is equivalent to 10^{-6} moles/L. These examples demonstrate that when the pH of the processed food increases, the concentration of hydrogen ions drops (Zhang et al, 2022). pH sensitivity of different microorganisms like fungi and bacteria may vary depending on the type of species. Extremely low or very high pH values inhibit microbial development. No unprocessed food has a pH value high enough to provide considerable preservation benefits (Samaranayake & Sastry, 2013). Many processed foods have pH levels low enough to provide some protection against microbial development. However, very few foods have pH levels low enough to entirely block the development of any spoilage bacteria. Almost all foods require a mix of microbial controls to help preserve them, including heat processing, refrigeration or freezing, or drying (Reineke, Mathys, & Knorr, 2011).

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For fresh fish, the normal pH value lies between 7.0 and 7.3, but this value drops significantly after death when the fish undergoes rigor mortis and glycogen is converted to lactic acid. The postmortem pH of most fish ranges between 6.0 and 6.8 (Limpan, et al., 2010). Postmortem pH of fish muscle is frequently evaluated during muscle conversion of meat since the pH value at the time of slaughter, the immediate decline of pH, and the ultimate pH after rigor mortis will directly impact the quality of the fish meat (Lawrie & Ledward, 2006). In farmed fish, postmortem muscle pH testing is often used in investigations on how pre-slaughter management affects the development of rigor mortis and the quality of marinated fish products (Skjold et al., 2020).

The pH of any fish product is frequently measured by directly introducing a pH electrode into the fish muscle. Alternatively, a muscle sample is homogenized in an aqueous liquid or a minced sample that may be combined with a liquid, and the pH is measured in the suspension using a regular pH meter (Andrés-Bello et al., 2013). When this latter method was developed many decades ago, it was advised to mince fish muscle with the presence of sodium iodoacetate concentrations to completely prevent glycolysis by inhibiting glyceraldehyde-3-phosphate dehydrogenase. When evaluating the pH of fish muscle, the addition of this enzyme inhibitor during homogenization is required since the mincing process increases glycolysis and the breakdown of adenosine triphosphate (ATP) and adenosine diphosphate (ADP) (Reineke et al., 2011).

According to Essid et al. (2020) the pH value of any marinated fish products should not be more than 4.8, and any fish products that exceed the limit are on the threshold of spoilage. In the study of Gülderen and Baştürk (2018), they assess the sensory and chemical changes of catfish fillets marinated in oil and tomato sauce and packed in an airtight bag. pH value was one of the parameters measured using HANNA model Microprocessor pH meter and recorded during the 200 day of storage period at a temperature of -4 °C. Values recorded during the homogenization process clearly stated that the marinated catfish fillets did not exceed the limit of what should be the pH value of marinated fish products.

However, Szymczak et al. (2020) stated that there are times the pH value of marinated fish might reach a value beyond the limit but is still considered safe to be consumed depending on the marinades used. This explains the study conducted by Khalafalla, Ali, and Hassan (2015) wherein they marinated 50 samples of Nile tilapia fillets using sunflower oil, acetic acid, with thyme or rosemary extract. The result showed that after 18 days of refrigerated storage, the Nile tilapia fillets marinated in thyme extract achieved a pH value of 5.2 using pH-meter (350 Jenway pH meter, UK), which exceeds the permissible limit. However, samples of the same marinade show good and acceptable sensorial properties based on the sensory evaluation conducted. According to Pattnaik and Mishra (2020), high concentration of polyunsaturated fatty acid in sunflower oil prompts oxidative degradation in marinated fish. However, the presence of thyme extract in any processed fish products imposes antibacterial and antioxidant benefits thereby preserving its quality due to carvacrol and thymol compounds in thyme extract that are hydrophobic compounds that dissolve in the hydrophobic domain of cytoplasmic membrane in bacterial cells. They cause an increase in the permeability to ATP that results in lethal damage to the bacterial cell (Burt, 2004). The study of Pattnaik and Mishra (2020) proves that pH value of marinated fish products should not be the only basis of assessing its quality, it should be supported by other parameters like sensory evaluation and other chemical tests.

The pH of fish varies depending on the season and species, and there are also differences based on the size of the fish. Smaller fish have higher pH values than larger fish, and the pH value in living fish tissue is near neutral (Gülderen & Baştürk, 2018). Kocatepe et al. (2019) investigated the changes happen on the pH value of anchovy marinated in vinegar alcohol, citric acid, and brine solution using digital pH meter (WTW Multi 340i). According to Shim, Mok, Jeong, Park, and Jang (2022), the pH value of raw anchovy lies between 8.5 – 9.5, and this value changes depending on the processing method applied. Based on the results obtained in the study of Kocatepe et al. (2019), the pH value of anchovy significantly dropped as they recorded a pH value of 4.7 which was still below the limit.

On the other hand, Cunha, Gadelha, Mello, Marmelo, Marques, and Fernandes (2022) used European seabass in their marinating experiment. Green tea marinade was utilized as a marinating agent during the 30 days of refrigerated storage. According to Poli et al. (2006), the average pH value of fresh European seabass is 6.43, and further processing will change its initial value. Based on the results obtained by the previously mentioned study, they recorded a significant decrease in the pH of marinated samples with a value of 4.3, this means that the values obtained were far from the limit of what should be the pH value of marinated fish products (Cunha et al., 2022). Table 6 shows different studies conducted to identify the pH value of marinated fish as well as the method or equipment used.

Table 6. Summary of studies that identify the pH value of marinated fish.

FISH	MARINADE USED	pH VALUE OF THE MARINATED PRODUCT	METHOD/ EQUIPMENT USED	REFERENCE
Nile tilapia	Marinade with thyme extract	5.2	pH-meter (350 Jenway pH meter, UK)	Khalafalla et al. (2015)
	Marinade with rosemary extract	4.6		
Anchovy	Marinade made up of vinegar alcohol, citric acid, and brine solution	4.7	digital pH meter (WTW Multi 340i)	Kocatepe et al. (2019)

Thiobarbituric acid reactive substance

TBARS is often used as a biomarker of lipid oxidation, specifically in meat and fish products (Papastergiadis et al., 2012). This process is often carried out in either direct extraction or distillation. The direct extraction approach applies to fresh meat and fish, and it includes macerating the material in a 7.5% solution of trichloroacetic acid (TCA). After filtering the extract, an aliquot is reacted with thiobarbituric acid in a boiling water bath for 35 minutes (Zhang et al., 2019). After cooling, the solutions are read against the reagent blank and compared to standards produced from 1,1,3,3 tetraethoxypropane (Xiong, et al., 2015). A plot of microgram malondialdehyde against absorbance is used to determine TBARS, which is reported as mg MDA/kg (Papastergiadis et al., 2012).

A distillation process may be used to analyze fish samples with a high fat content when turbidity is a concern. An aliquot is distilled at a regulated pace after being extracted in TCA and centrifuged until a predetermined volume is obtained. The distillate is then taken for reaction with thiobarbituric acid. The recovery of malondialdehyde using this procedure will be incomplete (Zhang et al., 2019). Thus, the standards must also be distilled. Distillation may also be used to extract oil and fats, as well as lipid extracts from fish samples (Ghani et al., 2017).

So far, no solid and proven data were recorded about the relationship between thiobarbituric acid reactive substance and sensory quality of fish. However, in the study conducted by Aubourg (2005), a significant relationship between the thiobarbituric acid reactive substance and rancidity rating was discovered in Coho salmon during the 14 days of cold storage. On the other side, an increase in thiobarbituric acid reactive substance of frozen Baltic cod and herring, mackerel, horse mackerel, and hake were not accompanied by the formation of rancid taste and odor during the 21 days of refrigerated storage (Rode & Hovda, 2016). In the first study, lipid hydrolysis was shown to have a stronger association with rancidity development than oxidation. In the second study, it was proposed that the presence of interfering components like protein may impact the detection of thiobarbituric. Both investigations found out that environmental conditions had an impact on fish shelf life as measured by sensory quality and chemical marker levels, including thiobarbituric acid due to differences in moisture, protein, and fat content. Fish quality degradation can also be caused by spoilage microorganisms that can only be measured by total volatile nitrogen (Idakwo et al., 2016).

In processed fish products, the acceptable consumption level is up to 8 mg MDA/ kg, while marinated fish with a TBA value of less than 3 mg MDA/kg are evaluated as good quality (Essid et al., 2020). This value is often influenced by the fish species used, handling procedure, storage condition, and marinating ingredients used (Testa, et al., 2019). On the marinating trials conducted by Phung, Sunisa, and Worapong (2019), they evaluated the effects of Vietnamese tamarind fish sauce enriched with iron and zinc to the quality and shelf life of green mussel. In this study they also used modified atmosphere packaging in storing the samples in a temperature below 4°C. According to Spencer (2005) the imposition of a gas atmosphere often includes an inert gas, such as nitrogen, mixed with an antimicrobial active gas, such as carbon dioxide, in a packed fish product to increase its shelf life is known as modified atmosphere packaging (MAP). This method of packaging may dramatically increase the shelf life of fish products, extending the distribution chain and reducing the requirement for centralized production (Bouletis et al., 2017).

Modified atmosphere packaging act as an additional barrier against spoiling, increasing shelf life and fish product safety. It is also affordable, simple to apply, and suited for a wide range of packing machines and manufacturing facilities (Silbande et al., 2016). Based on the result of the experiment conducted by Phung, Sunisa, and Worapong (2019), marinated green mussel showed an increasing value of thiobarbituric acid reactive substance all throughout the storage period, samples without modified atmosphere packaging obtained a 8.45 mg MDA/kg value that exceeds the acceptable consumption level, while samples stored in a modified atmosphere packaging showed a 6.58 mg MDA /kg value that did not exceed the acceptable consumption level.

Thiobarbituric acid reactive substance is one of the criteria on identifying lipid oxidation in most fish processed products (Zhang et al., 2019). Lipid oxidation often causes bitter taste and yellow-brown color formation in marinated fish products, this phenomenon is causing problems in the fish processing industry because it limits the shelf life of fish and causes loss of quality (Halamíčkov & Malota. 2010). To prevent this to happen, antioxidants in the form of marinade additives were applied in marinating procedure (Fu et al., 2015). Table 7 shows the class of antioxidants that can be used in marinating any fish products and their examples with corresponding functions.

In today's time, the use of synthetic antioxidants have been widely utilized to control lipid oxidation in marinated fish, as it yields a longer shelf life than herbs and spices alone. However, other studies suggest that the use of synthetic substances imposes risks and negative effects on human health (Suh et al., 2005). In the study conducted by Sutanto and Purwanto (2019), they used *tert*-butylhydroquinone and rosemary extract in marinating the grey trout fillet. *Tert*-butylhydroquinone is a synthetic food additive that is used to enhance the shelf life and prevent rancidity of any food products. It's a light-colored crystalline substance with a little odor that serves as an antioxidant to prevent processed fish products containing iron from discoloration (Gharavi, Haggarty, & El-Kadi, 2007). It is frequently used in conjunction with other synthetic additives such as propyl gallate, butylated hydroxyanisole (BHA), and butylated hydroxytoluene (BHT) (Pu et al., 2018). After the marinating trials conducted by Sutanto and Purwanto (2019), grey trout fillets showed acceptable sensorial properties, particularly on their texture and color; the presence of *tert*-butylhydroquinone preserves the natural color of the samples. The authors stated that the thiobarbituric acid reactive substance of the samples was significantly kept below the acceptable consumption level with an average value of 5.67 mg MDA/kg. They also added that the shelf life of marinated grey trout may extend for at least 7 months if stored in a cold storage.

Despite the preservation benefit of *tert*-butylhydroquinone, this synthetic substance still poses a threat to public health (Eskandani, Hamishehkar, & Dolatabadi, 2014). According to Khezerlou et al. (2022), too much consumption of food products that contain *tert*-butylhydroquinone, impose a long-term health issue, and to some, records of acquiring chronic diseases like cancer and liver infection were reported. Table 8 shows the summary of different studies that identify the TBARS of marinated fish and the equipment or procedure used in analyzing.

Table 7. Class of antioxidants and their preservative function (Embuscado, 2015)

CLASS OF ANTIOXIDANTS	EXAMPLES	FUNCTION
Free radical scavengers	BHA (Butylated hydroxyanisole) BHT (Butylated hydroxytoluene) TBHQ (tert-Butylhydroquinone) Propyl gallate Tocopherols Extracts from spices and herbs (rosemary, clove, sage, oregano)	Block free radicals by donating a hydrogen atom
Oxygen scavenger	Ascorbic acid Erythorbic acid Ascorbates Sulphites, bisulphites Ascorbic palmitate	React with oxygen
Chelating agents	Citric acid EDTA (Ethylenediaminetetraacetic acid) Phosphates	Sequester/ chelate metal ions capable of catalyzing oxidation

Table 8. Summary of studies that identify the TBARS of marinated fish

FISH	MARINADE USED	TBARS VALUE OF THE MARINATED PRODUCT	EQUIPMENT/ PROCEDURE USED	REFERENCE
Green mussels	Vietnamese tamarind fish sauce	8.45 mg MDA/kg	Microsomal lipid peroxidation	Phung et al. (2019)
Grey trout	Marinade with *tert*-butylhydroquinone and rosemary extract	5.67 mg MDA/kg	Isocratic elution	Sutanto & Purwanto (2019)

Total volatile base nitrogen

TVBN is composed of three volatile compounds such as ammonia, dimethylamine, and trimethylamine, these compounds are primarily responsible for the spoilage of fish and seafood and give fish a strong and unpleasant odor (Idakwo et al., 2016). The TVBN value, especially in the case of marine fish and shellfish, is an essential indicator of freshness since fish in particular produces basic nitrogen during decomposition (Castro et al., 2012). Trimethylamine (TMA) levels rise during spoilage. After the death of fish, the activity of spoilage bacteria rises increasing the reduction of trimethylamine oxide (TMAO) to trimethylamine. Trimethylamine oxide is the primary source of dimethylamine (DMA) and trimethylamine in fresh and processed fisheries products (Neira et al., 2019). Post-mortem degradation of trimethylamine oxide and the consequent buildup of volatile amines contribute significantly to the quality loss of fish products to the disagreeable scents associated with the breakdown products. Bacterial spoilage is responsible for the generation of trimethylamine from trimethylamine oxide reduction (Nowsad et al., 2015).

The traditional technique for measuring TVBN levels in fish muscle involves extracting volatile bases using a perchloric acid solution, followed by steam distillation of the extract, which is then collected in boric acid and titrated against standard hydrochloric acid (Bhadra et al., 2015). However, the existing approach for TVBN measurement is not only damaging, time-consuming, and inefficient, but it is also incompatible with modern industrial processing and detecting targets (Cheng, et al., 2017). As a result, it is critical to look for fast, accurate, non-destructive, and objective TVB-N level detection techniques for assessing protein degradation (Wang et al., 2019).

Hyperspectral imaging technique combined with multivariate data analysis is an alternative, rapid, and non-destructive tool that has gradually developed for the inspection of the quality and safety of various food products including fish muscle by integrating spectroscopy with imaging or computer vision into one system (Yu et al., 2021). A typical hyperspectral imaging system creates a spatial map of sample spectral variance. The hyperspectral picture includes a three-dimensional dataset known as hypercube I (x, y, λ) with one spectral dimension and two spatial dimensions. Furthermore, chemometric approaches such as partial least squares regression (PLSR) and least squares support vector machines (LS-SVM) and others are necessary to improve the use of hyperspectral imaging (Wang et al., 2019). However, this technique has low accuracy and reliability, making it not applicable for online and real-time detection of chemical changes in fish muscle (Khoshnoudi-Nia & Moosavi-Nasab, 2020). Figure 2 shows the equipment used in hyperspectral imaging to identify the TVBN value of marinated fish.

According to Kumar and Mathew (2016), the maximum permissible limit of TVBN value in fish and any processed fish products is 35 mg N/100 g, the value of fish products that exceed this limit is considered to be in a spoilage state. This value is often affected by the fish species, ingredients used, and handling procedure (Di Toro et al., 2019). Based on the study conducted by Sorio and Inolino (2018) the TVBN value of green mussels marinated in 66% vinegar and 2% salt was significantly low, accounting for an average value of 30.16mg N/100g after a chilled storage for 28 days. Other than that, Tomac and Yeannes (2015) investigated the quality changes of marinated anchovy using gamma-irradiated marinades. Food irradiation is a physical therapy that involves direct radiation exposure. Exposure to electron or electromagnetic radiation for long-term preservation and quality and safety enhancement (Aly et al., 2014). This method uses Cobalt-60 which emits excessively energetic electromagnetic -rays. Radiation causes DNA molecules to expand and break along the chain, preventing them from functioning normally. As a result, the parasites and bacteria that have been damaged by the radiation lose their ability to reproduce and eventually die (Arvanitoyannis & Tserkezou, 2014). Therefore, food irradiation provides safety and extends the shelf life of fisheries products because of its high effectiveness in inactivating pathogenic and spoilage microorganisms without deteriorating product quality (Huque, Islamm, & Khatun, 2013).

The effect of irradiation on microbial population and composition is dependent on irradiation dosage, storage temperature, storage condition, and fish species. As a preservation method used for long periods of storage, freezing limits microbial development and metabolic changes in fish (Hocaoğlu, et al., 2012). When irradiation is used in conjunction with freezing, the irradiation doses can be lowered by synergistic action without affecting product quality (Badr, 2012). In the previously mentioned study, Tomac and Yeannes (2015) observed a slow increase in the TVBN value of gamma-irradiated samples (28 mg N/100 g) compared to untreated samples, this proves that gamma irradiation is effective at inhibiting the growth of spoilage microorganisms in fish. However, the authors also explained that the slow increase in TVBN value of gamma-irradiated samples is due to little effect of irradiation in the enzymatic activity of fish that produced dimethylamine. Table 9 shows the summary of different studies that identify the TVBN of marinated fish as well as the equipment and/ or procedure used.

Table 9. Summary of studies that identify the total volatile base nitrogen (TVBN) of marinated fish.

FISH	MARINADE USED	TVBN VALUE OF MARINATED PRODUCT	EQUIPMENT/ PROCEDURE USED	REFERENCE
Green mussels	Marinade made up of vinegar and salt concentration	30.16 mg N/100 g	Standard Conway micro diffusion method	Sorio & Inolino (2018)
Anchovy	Gamma irradiated marinade	28 mg N/100 g	Direct distillation	Tomac & Yeannes (2015)

Safety Challenges and Precautions in Marinating Fish

Despite the preservation and nutritional benefits of marinating fish, the improper way of implementing the process can also lead to food hazards (Arason et al., 2014). According to Vidaček and Janči (2016), data on food borne diseases and intoxication are linked to marination in Switzerland as they examined 2000 fish meats due the possible presence of *Listeria monocytogenes* which weakens the immune system of the victim. According to them, the inspection lasted for 9 years to ensure the total cleanliness and safeness of the marinated fish.

Some of the hazards like biotoxins, parasites, and chemical contaminants can be obtained from the raw material, or the fish used in marinating. Therefore, handlers should check if the raw material originates from a safe source. And similar principle should be applied in choosing possible marinating ingredients (Köse, 2010). To prevent or at least delay the formation and growth of spoilage bacteria, maintaining the acidic property of fish marinades is a must. Thus, the standard concentration of fish marinades must be 6-18% salt and 0.3-2% acetic acid, and a 6% increase in the concentration of salt was reported mainly in Western countries (Di Toro et al., 2019). Histamine is a toxic metabolite produced by histamine-producing bacteria during spoilage and fermentation of fish and fish products. The skin, gills, and intestines of freshly caught fish naturally contain many microorganisms that produce histamine. The amino acid histidine that is naturally found in fish is converted into histamine by histidine decarboxylase (HDC) enzymes, which are produced by histamine-producing bacteria as they grow. In order to avoid histamine formation among fresh and processed fish, keeping the storage condition at a low temperature is a must (Köse, 2010). According to Arason et al. (2014) the ideal temperature to keep any processed fish product free from histamine formation is below 0°C.

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