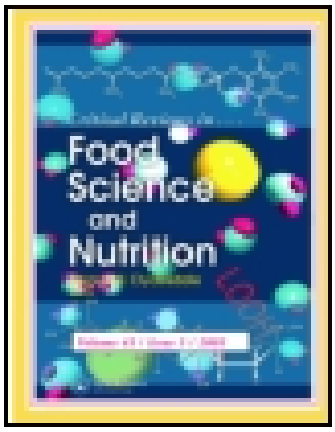

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Quality Evaluation of Fish and Other Seafood by Traditional and Nondestructive Instrumental Methods: Advantages and Limitations

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Quality evaluation of fish and other seafood by traditional and nondestructive instrumental methods: Advantages and limitations

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Abstract:

Although being one of the most vulnerable and perishable products, fish and other seafoods provide a wide range of health-promoting compounds. Recently, the growing interest of consumers in food quality and safety issues has contributed to the increasing demand for sensitive and rapid analytical technologies. Several traditional physicochemical, textural, sensory, and electrical methods have been used to evaluate freshness and authentication of fish and other seafood products. Despite the importance of these standard methods, they are expensive and time-consuming, and often susceptible to large sources of variation. Recently, spectroscopic methods and other emerging techniques have shown great potential due to speed of analysis, minimal sample preparation, high repeatability, low cost, and, most of all, the fact that these techniques are noninvasive and nondestructive and, therefore, could be applied to any on-line monitoring system.

This review describes firstly and briefly the basic principles of multivariate data analysis, followed by the most commonly traditional methods used for the determination of the freshness and authenticity of fish and other seafood products. A special focus is put on the use of rapid and nondestructive techniques (spectroscopic techniques and instrumental sensors) to address several issues related to the quality of these products. Moreover, the advantages and limitations of each technique is reviewed and some perspectives are also given.

Keywords spectroscopy, fish and seafoods, chemometry, freshness, authenticity

Introduction

Fish and other seafood products play a useful role in a nutritional and balanced diet, and their consumption has long been associated with several health benefits. Indeed, these products provide a number of nutrients, including protein, long-chain omega-3 polyunsaturated fatty acids such as eicosapentaenoic and docosahexaenoic acids, and a number of vitamins and minerals (Weichselbaum et al., 2013). However, fish and other seafoods are highly perishable food products, due to their high water activity (a_w), neutral pH, low content of connective tissue, and the presence of autolytic enzymes which cause rapid development of undesirable odors and flavors. So adequate treatment is required to maintain the quality of these vulnerable products and reduce their spoilage as much as possible.

Public interest in food quality and methods of production has increased significantly in recent decades, due in part to changes in eating habits, consumer behavior, and the increased industrialization and globalization of food supply chains (Christensen et al., 2006; Karoui et al., 2010). Quality is frequently described using terms related to nutritional, microbiological, biochemical, and physicochemical characteristics alone, but none of these terms serve as adequate indices of quality and, therefore, consumer acceptability must be included. However, it is exceptionally difficult and complicated to define quality precisely in such a way as to satisfy everyone. The quality of fish is even a more complex concept as it is affected by several factors such as species, age, proximate composition, fishing area, season, and animal nutritional status. Nevertheless, fish freshness is considered as the most important quality parameter since it is directly related to the sensory attributes perceived by consumers such as appearance, texture, odor, and taste. For all kinds of seafood products, freshness is essential for quality of the final

product, since this quality parameter is affected by several factors, such as rigor mortis, autolysis processes, and microbiological spoilage after death (Alasalvar et al., 2011; Cheng et al., 2013a; Cheng et al., 2014).

Nowadays, the authentication of seafood products is a major concern in order to: i) assure the traceability system from fish to fork; and ii) ensure that food products are correctly labeled in terms of which animals are actually processed for consumption. Illegal, unreported and unregulated fishing is a serious problem that leads to depletion of fishing stocks, loss of money and lack of consumer protection (Lavilla et al., 2013). Although relevant authenticity issues of fish and other seafoods include species, geographical origin, and production method (i.e., wild/farmed), other factors such as processing conditions (fresh/frozen thawed fish), substitutions, and so on could be considered in this context.

Determination of the quality of fish and other seafoods has been carried out with several analytical methods. The physicochemical methods used for quality evaluation of fish and other seafoods are based on the determination of the total volatile basic nitrogen (TVB-N) and other volatiles amines, as well as biogenic amines (Castro et al., 2006; Etienne, 2005; Onal et al., 2013; Ozogul et al., 2008; Visciano et al., 2012). Additionally, fish and seafoods contain high levels of polyunsaturated fatty acids, making them more susceptible to oxidation reactions. Therefore, measurements of lipid oxidation products such as thiobarbituric acid reactive substances (TBARS) and peroxide value (PV) are commonly used as indicators of freshness of such products (Cheng et al., 2013a; Hong et al., 2013; Li et al., 2011; Tejada et al., 2007). Some other studies have considered the concentrations of adenosine triphosphate (ATP) and its

breakdown products as indicator of freshness in many fish species (Ocaño-Higuera et al., 2011; Li et al., 2011; Tejada et al., 2007; Watanabe et al., 2005).

With regard to sensory methods, the most commonly used methods for freshness determination of fish and other seafoods, they have been traditionally applied to determine some attributes (including appearance, color, odor, flavor, texture, and taste) perceived with the human senses (Bonilla et al., 2007; Sant'Ana et al., 2011). As it is a part of quality, texture is an extremely important property of fish muscle, for both raw and cooked. Therefore, texture measurements have been applied to monitor the quality of seafood products during processing, storage, and distribution (Barroso et al., 1998a; Casas et al., 2006; Coppes-Petricorena, 2011). Additionally, electrical properties, measured by Torrymeter and Fischtester, have been tested in several studies (Lougovois et al., 2003; Oehlenschlager, 2005; 2014).

Although the importance of the above-mentioned methods is undeniable, most of them are tedious and destructive, relatively expensive, time-consuming, and require highly skilled operators. In addition, the variation in texture properties of fish and other seafoods depend strongly on the fish muscle tissue structure. Recently, more attention has been paid to the development of noninvasive and nondestructive instrumental techniques such as infrared, fluorescence, nuclear magnetic resonance (NMR), and Raman spectroscopies, as well as some emerging techniques like instrumental sensors. These techniques are fast, of relatively low cost, environmentally friendly, and provide a great deal of information with only one test, making them suitable for on-line and/or at-line process control. Moreover, spectroscopic techniques often require little or no sample preparation and allow to avoid sample destruction (Cheng et al., 2013b; Karoui et al., 2006c; 2010).

There has never been a thorough review on the use of jointly traditional and spectroscopic methods for the determination of the freshness, authenticity, and other quality parameters in fish and other seafoods (such as oysters, shrimps, and so on). Thus, the present review paper will provide a comprehensive overview of the applications of different traditional and instrumental techniques, in combination with multivariate data analysis, to determine different quality aspects of fish and other seafoods. Actual examples illustrating the utilization of these techniques in both laboratory and industrial environments will be discussed, as well as their advantages and disadvantages.

Multivariate Data Analysis

Chemometrics is related to the application of mathematical and statistical methods in order to process data acquired on a food product in an optimal way. These techniques allow optimal application of the analytical methods, in particular spectroscopic ones, through the extraction and interpretation of valuable information from large and complex data sets, identification of patterns in the data, and development of calibration models in many analytical fields (Cheng et al., 2013b; Karoui et al., 2006a; b; 2007a; b). These powerful methods and the computer technology necessary to use them have only become readily available in recent years; their application has become a significant feature for the analytical techniques used to evaluate the quality of fish and other seafoods. A broad range of chemometric tools is now available including data reduction tools, regression techniques, and classification methods (Cheng et al., 2013b; Dai et al., 2014; Karoui and Blecker, 2011; Karoui et al., 2010).

The best known and most widely used variable-reduction method is principal component analysis (PCA). The PCA is a powerful and versatile method capable of providing an overview of complex multivariate data. It could reveal the relations between variables and relations between samples, allowing the detection of outliers (Bro and Smilde, 2014). This technique decomposes the data matrix with *n* rows (samples) and *p* columns (variables) into the product of a scores matrix, with *n* rows (samples) and $d<p$ columns (principal components, PCs), and a loadings matrix. The scores are the position of the samples in the space of the PCs, while the loadings are the contributions of the original variables to the PCs. All PCs are mutually orthogonal, and each successive PC contains less of the total variability of the initial data set.

The PCA can always offer an overview of the problem studied and often allows the drawing of significant conclusions and for decisions to be made on the basis of the observed results. Furthermore, it constitutes the basis for other, more complex, pattern recognition techniques (Karoui et al., 2010; Oliveri and Forina, 2012).

Exploratory techniques for data analysis, such as PCA, are unsupervised methods, meaning that they just show the data as they are. Conversely, supervised chemometric methods, such as discriminant analysis, look to determine features within data, explicitly oriented to address particular issues (Oliveri and Forina, 2012). A wide variety of discriminant analysis have been investigated for this purpose including linear discriminant analysis (LDA), factorial discriminate analysis (FDA), partial least squares discriminant analysis (PLS-DA), quadratic discriminant analysis (QDA), partial least-squares regression (PLSR), and so on (Dai et al., 2014; Oliveri and Forina, 2012).

An example of a popular supervised classification method is soft independent modeling of class analogy (SIMCA). This method builds class models based on PCA performed using only the samples of the category studied, generally after within-class autoscaling or centering. In more detail, SIMCA models are defined by the range of the sample scores on a selected number of low-order PCs, and models therefore correspond to rectangles (2 PCs), parallelepipeds (3 PCs), or hyper-parallelepipeds (more than 3 PCs) referred to as the multidimensional boxes of SIMCA inner space (Oliveri and Forina, 2012).

In the case of complex data sets, the above-mentioned statistical methods could not produce robust and efficient predictive models. To remedy this, several methods based on the concepts of statistical learning theory, including support vector machine (SVMs), artificial neural network (ANN), probabilistic neural networks (PNN), Bayesian belief networks (BBN), and others have been proposed. Moreover, other sophisticated chemometric methods such as PARAllel FACtor analysis (PARAFAC), have received increasing attention over the past few years, especially with the development of fluorescence excitation-emission matrix (EEM). This technique enables the decomposition of EEM matrices into their underlying chemical components, leading to the mathematical identification and quantification of the independent fluorophores (Murphy et al., 2013). Currently, commercial software packages, such as Matlab, Unscrambler, and others are available to manipulate data obtained from spectroscopic techniques (Pu et al., 2015).

Traditional Techniques Used for the Determination of the Quality of Fish and Other Seafoods

Physicochemical Analysis

It is well-known that the quality of fish degrades after death due to chemical reactions, including formation of volatile and biogenic amines as well as changes in other physicochemical parameters such as pH, aw, ATP-related compounds, and K value. Many of these parameters have been selected as tools to evaluate the quality of fish and other seafoods. **Table 1** summarizes some relevant topics about the most common physicochemical and other traditional methods cited in the literature of this field.

Amine compounds, which are formed in seafood products as a result of muscle decomposition, appeared to be the first described ones in the literature. They could be generated by enzymatic reactions, lipid autoxidation, and/or microbial actions. Volatile amines are the most characteristic molecules responsible for odor and taste present in fish after several days of catch, and they are commonly used as indices for assessing fish quality (Etienne, 2005).

TVB-N has been used as an indicator of spoilage of some fish species such as red fish, flat fish, gadoids, hake, and Atlantic salmon, although this parameter seemed not to be the major cause of spoilage (Etienne, 2005). For example, TVB-N values below the upper limit of acceptability (35–40 mg/100 g of fish muscle) were observed in ungutted white grouper fish kept in ice at chill temperature (4 °C), while unacceptable values were obtained from sensory evaluation (Ozogul et al., 2008). One of the main conclusions of this study was that TVB-N levels could not be considered as a reliable freshness indicator of the investigated fish samples. Moreover, some disagreements among several of the published results have been observed since the amount of TVB-N seemed to vary according to fish species. For example, values of 26.19 and 37.96 mg/100 g were observed after 8 days of storage in ice of red mullet and goldband goatfish,

respectively (Ozyurt et al., 2009). The obtained results were in accordance with those of Ocaño-Higuera et al. (2011) who pointed out an increase in the TVB-N values of ray samples since it passed from 21 to 54 mg/100 g of ray muscle during 18 days of ice storage. However, in another study, conducted by Castro et al. (2006), the authors did not observe any change in the levels of TVB-N during the first 2 weeks storage of the European sea bass in ice, and concluded that this indicator was not reliable for the determination of freshness for this fish species.

From the aforementioned results, it could be concluded that volatile amine levels change at variable rates depending on numerous factors, such as fish species, storage conditions, and so on. Consequently, precautions should be taken when using such indicators for determining freshness and predicting the shelf-life of fish and other seafood products.

Biogenic amines are found at low levels in fresh fish tissues, but their formation in larger quantities is associated with microbial decomposition of fish muscles. In spoiling fish, biogenic amines are produced from free amino acids liberated from proteins and peptides. The high content of proteins in the fish meat represents a risk of rapid formation of biogenic amines that are biologically active molecules having aliphatic, aromatic, or heterocyclic structures (Onal et al., 2013). Identification and quantification of biogenic amines in food samples are of crucial importance because of their toxicological risk and also their use as indicators of food quality and freshness. It is well-known that histamine, cadaverine, tyramine, and agmatine are produced from the decarboxylation of histidine, lysine, tyrosine, and arginine, respectively.

A wide variety of procedures for the determination of biogenic amines has been published in the literature. These include colorimetric (Patange et al., 2005), enzymatic (Lange and Wittmann, 2002), and chromatographic (Onal et al., 2013) methods. However, each technique has its

advantages and drawbacks, and there is no unique standard method to assess the quality of fish and other seafood products.

As observed for TVB-N, the amount of biogenic amines increases with storage time. For example, biogenic amines and ammonia amounts in red mullet and goldband goatfish kept in ice increased significantly during 11 days of storage (Ozyurt et al., 2009). Agmatine, serotonin, histamine, and dopamine became the dominant amines in red mullet, reaching values of 7.30, 5.97, 2.52, and 2.31 mg/100 g, respectively, while concentrations of dominant amines for goldband goatfish were of 4.37, 3.88, 3.38, and 2.00 mg/100 g for histamine, agmatine, dopamine, and putrescine, respectively.

The impact of technological process on the formation of biogenic amines has been investigated by several authors. For example, the effects of different freezing treatments on the formation of biogenic amines of cultured bighead carp heads were determined in a recent study (Hong et al., 2013). The authors noticed that fish samples frozen under different freezing temperatures had significant lower values of spermine and spermidine than the control. In another approach, and in order to prolong the shelf-life of fish samples, radiation technology was applied to trout meat (Krizek et al., 2012). Application of high-energy electron beam irradiation at doses within the range of 0.75 and 1.0 kilogray prolonged the shelf-life of trout meat by up to 70 and 98 days, respectively, which was explained by the reduction of biogenic amine levels in the treated samples.

On the basis of the aforementioned studied, it is evident that several factors, such as storage time and condition, as well as method used for the determination of biogenic amines, could make the correlation between the concentration of these amines and the degree of fish decomposition

doubtful. Thus, the use of biogenic amines as a freshness index of fish might be considered not appropriate.

In addition to volatile and biogenic amines, other physicochemical parameters, namely, ATP-related compounds and K value, lipid oxidation indices**,** pH, salt content, aw, and more, seem to play a major role in quality assessment, and thus have been proposed as tools to evaluate the quality of fish and other seafoods. A recent study was conducted with the aim of studying the kinetics of lipid oxidation occurring during postmortem storage in different batches of Atlantic mackerel caught during the spring and summer periods (Maestre et al., 2011). It was evidenced that the onset of lipid oxidation was related to the initial muscle composition, and a good correlation between, on the one hand, shelf-life and water content (R= 0.78) and, on the other hand, shelf-life and total lipid contents (R= 0.76) was found. Then, the authors attempted to explain the onset of lipid oxidation considering the whole composition of mackerel by using forward stepwise multivariate regression models. Using the variables which contribute mostly to lipid oxidation (that are PUFAs followed by the contents of total iron, hemoglobin, and ascorbic acid) in their model, the authors achieved prediction of shelf-life with very high accuracy (R^2 = 0.99).

One of the most important postmortem biochemical changes in the muscle of marine organism is ATP degradation and its breakdown products, which have been widely studied and used as an indicator of freshness and shelf-life of fish muscles at different stages: rigor mortis, dissolution of rigor mortis, autolysis, and bacterial spoilage. It is well-documented that after the death, fish muscle undergoes postmortem changes, caused by the decomposition of ATP into a number of metabolites, including adenosine diphosphate (ADP), adenosine monophosphate (AMP), inosine

monophosphate (IMP), inosine (HxR), and hypoxanthine (Hx) (Cheng et al., 2013a; Li et al., 2011; Ocaño-Higuera et al., 2011; Watanabe et al., 2005). K value is expressed as the percentage of the total amount of HxR and Hx to that of ATP and its related compounds in fish muscle. Measurement of the K values is considered as one of the useful techniques for the evaluation of fish freshness, since high correlation was found between this index and storage time in different fish species. For example, Ocaño-Higuera et al. (2011) reported a significant and exponential increase of K value in ray fish muscle, which passed from 4.7% (day 0) to 47.5% (days 18). In another study by Tejada et al. (2007), different indices (such as Torrymeter readings, TMAO, TMA-N, TBARS, and dielectric measurements), in addition to k value, were investigated to monitor changes occurring in farmed Senegalese sole during ice storage. The K value was found to be the most effective freshness indicator, since a linear correlation with storage time was observed, confirming the possibility of using this indicator for monitoring fish freshness during storage.

It was reported in several studies that the ATP and some of its degradation products (ADP and AMP) decrease rapidly and nearly become nil after 24 h of storage at 0 °C, while the IMP level increases sharply at approximately 5–24 h after death and then decreases gradually during storage (Ocaño-Higuera et al., 2011; Li et al., 2011; Watanabe et al., 2005). Therefore, another indicator, called K_I value could be calculated, based on the IMP, HxR, and Hx. This indicator was found to correlate with storage time for yellow grouper (Li et al., 2011), and the remaining shelf-life days of sashimi (Watanabe et al., 2005), indicating that K_I value provides a useful indication of freshness.

One of the main disadvantages of the use of K and K_I values is their dependence on the ATP rate decomposition and the degradation pattern of the different resulting metabolites, which in turn, depend on the species. Therefore, it is important to keep in mind that these indicators must be calculated for each kind of fish and seafood product.

Food authenticity issues in the form of adulteration and improper description have been around for a long time and probably for as long as food has been offered for sale. In fish and other seafood sectors, most of the efforts have been directed to authenticate the species and to determine the geographic origin. However, up to date, few markers can be used efficiently to unequivocally establish specimens as the production method (wild / farmed) or the geographical origin of fish and other seafoods. For example, total fat contents and long-chain fatty acids including, saturated, monounsaturated, and polyunsaturated fatty acids, in extracted fish oil have been used for authentication purposes (Lavilla et al., 2013). In order to differentiate between wild and cultured species, Tritt et al. (2005) examined fatty acid composition of juvenile largemouth bass, white crappies, and black crappies. By applying a series of chemometric tools, namely, analysis of variance, PCA, and QDA to 4 fatty acids (linoleic acid: 18:2n-6, linolenic acid: 18:3n-3, arachidonic acid: 20:4n-6, and docosahexaenoic acid: 22:6n3), linoleic acid was found to be the primary fatty acid that could be used to differentiate juvenile wild from cultured fishes. In addition, the use of the 4 fatty acids allowed to classify correctly 90 of 91 juvenile fishes as wild or cultured; 32 of 37 wild juvenile fishes originating from the same reservoir were differentiated by species. To test the accuracy of the established model, the authors used a training data set (n = 8) and 100% accuracy was obtained according to species, source, or origin.

Although the physicochemical analyses are considered as reference methods, providing accurate and reliable results on quality and authenticity of fish samples, they are time-consuming and need a lot of polluting reagents, are relatively expensive, cannot be utilized at/on-line, and involve the use of chemicals and trained labor.

Sensory Analysis

Sensory analysis is the most common method used to evaluate fish freshness. Although all the developments occurring so far in instrumental methods, sensory methods remain the most satisfactory way to assess freshness of fish and other seafoods (Alasalvar et al., 2011; Green, 2011). These techniques are becoming increasingly important in market development and frequently are correlated with chemical, microbial, and physical assessment techniques. Fish and seafoods are different from all other food commodities in: i) method of harvesting; ii) fragility of the products during transport to processing sites; and iii) temperature dependency and variety of species. Therefore, particular attention should be paid to these problems when selecting sensory evaluation techniques. Depending on the research questions, different methods could be used. As an example, for studying the impact of storage conditions on both the quality and shelf-life of raw fish, the quality index method (QIM) is recommended. For other changes such as determination of the maximum storage time, descriptive methods can be used, such as quantitative descriptive analysis (QDA). In the case of cooked fish, the Torry scale is most frequently used in the industry for evaluating fish freshness (Green, 2011).

Morphological variations have been shown to be a valuable tool to describe changes occurring in shape features. Thus, Alasalvar et al. (2002) noticed fundamental differences in morphology

between farmed and wild sea bream, since the appearance of the latter was described to be more bleached greenish, had sharper dorsal fins, more scales, sharper teeth with greater height and conical edge, smaller bellies, and shorter tails compared to the former one. Wild sea bream had also a golden tape between the eyes and a reddish patch on the surface of the gill cover. However, in most of the cases, morphological differences between species of fish could not be detected, especially at juvenile stages. Consequently, a large number of sensory analysis techniques have been developed. One of the most interesting is QIM which is based on a scoring system of freshness and quality estimation of fish and seafoods. A score of 0 to 3 demerit (index) points is given for each quality parameter according to the specific parameter descriptions. The scores are summarized to give an overall sensory score, called Quality Index (QI) (Bonilla et al., 2007; Sant'Ana et al., 2011; Sveinsdottir et al., 2003).

Several authors have used the QIM for quality and shelf-life assessment of different fish species. For instance, a study was carried out to investigate the shelf-life and freshness quality of 2 fish species: red mullet and goldband goatfish belonging to the same family (Ozyurt et al., 2009). The QIM scheme consisted of 9 parameters which gave a total of 18 demerit points, describing 3 quality attributes (whole fish, eyes, and gills). The initial quality characteristics of the red mullet and goldband goatfish were found to be similar at the beginning of storage (very bright appearance, hard texture, bright and convex eyes, and fresh odor). Then the demerit points increased in the 2 species with storage time. Although the initial sensory scores of the 2 species were the same on day 0, the scores of goldband goatfish were found to be higher than those of red mullet during the storage period. The authors concluded that the sensory acceptability limit was 8 days for goldband goatfish and 11 days for red mullet. Difference in shelf-lives of the 2

species was confirmed by microbiological (TVC) and some chemical (pH, TVB-N, TBA, free fatty acids, PV, and biogenic amines) analyses.

The same approach was developed to predict the remaining shelf-life of farmed salmon kept in ice based on a total of 22 demerit points describing 11 sensory attributes for appearance and odor of skin, eyes, abdomen, gills, and texture (Sveinsdottir et al., 2003). Due to the biological variation between individual fish, the average QI was calculated from the assessment of five specimens, and it gave a high correlation (R^2 = 0.97) with storage time. Scores for all quality attributes increased with storage time, in particular those of skin mucus and odor which increased from about 0.5 to attain a maximum score of about 3. For very fresh salmon, the odor was described as fresh seaweed or cucumber, then became neutral and during the later stages it was described as sour and finally as rotten, due to the formation of short-chain fatty acids, alcohols, sulfur compounds, and amines. Then the authors applied the QDA approach to determine the maximum storage time of cooked salmon. For this purpose, specific terms were designated and categorized into 2 groups: positive and negative sensory parameters depending on whether the description concerned fresh salmon or salmon at the end of its storage time. From the obtained results, the authors concluded that the maximum storage life of salmon kept in ice was 20–21 ± 1.5 days.

In a similar study, sensory analysis was developed, including QIM and QDA techniques, to study raw cod fillets and to determine the shelf-life of the fish (Bonilla et al., 2007). In this study, the QIM scheme, based on a total of 18 demerit points, was developed including 8 sensory attributes. Again, the QI, which increased during storage time, was found to be linearly related to storage time in ice (R^2 = 0.99). As described in the previous study, the QDA method was used on cooked

fish samples to determine the maximum storage time. At the beginning of storage, small changes of positive attributes of odor and flavor (such as sweet, metallic) were perceived. After 7 days of storage, they were hardly detectable due to the increase of negative attributes (such as rotten, sour). As a result, maximum storage time of cod fillets kept in ice was estimated to be 8 days.

QIM schemes must be adapted to each species, incorporating their respective characteristics. Sant'Ana et al. (2011) developed a QIM scheme, consisting of 14 parameters, which described 6 quality attributes (appearance, texture, mouth, anal area, eyes, and gills) giving a total of 30 demerit points, for blackspot seabream stored in ice. As reported, obviously, the odor appeared to be one of the attributes that was mostly influenced by storage time. Indeed, at the beginning of storage, the skin odor was described as fresh or seaweedy, then the odor became neutral and after 12 days of storage in ice it was described as sour milky and then metallic during the later stages (18 days). The authors recommended that blackspot seabream should be rejected only after 12-13 days of storage in ice, mainly due to the presence of unpleasant odors in skin and gills.

The most common method used to determine cooked fish freshness is the Torry scheme. This technique is a 10-point scale originally developed to assess the eating qualities of cooked fish samples. Scores are given from 10 (very fresh in taste and odor) to 3 (spoiled). Scores below 3 are considered unnecessary as the fish is not fit for human consumption. In this context, a comparative study between the use of the Torry scheme for the sensory analysis of cooked anchovy, and QIM for the evaluation of raw fish was conducted by Pons-Sanchez-Cascado et al. (2006). The QIM scheme was based on a total of 23 demerit points describing 10 sensory attributes for general appearance, eyes, abdomen, gills, and flesh, while with the Torry scheme panelists were asked to score odor, texture, and taste using a 0–10 hedonic scale with 10 and 0

corresponding to the most liked and the least liked samples, respectively. The suitability of the 2 sensory schemes was evaluated by a receiver operating characteristic curve, and the values of the areas under the curves were estimated. The authors concluded that values over 0.51 for raw and lower than 7.1 for cooked anchovy, respectively, reached after 5 days of storage in ice, are indicators of lowest acceptability (Pons-Sanchez-Cascado et al., 2006).

On the basis of the aforementioned studies, it is evident that sensory methods offer immediate measurement of perceived attributes and provide information that may be of help for a better understanding of consumer responses. However, these methods have some disadvantages such as variations among individuals in the response of the same level of stimuli, which could contribute to a no-conclusive answer of the test. Moreover, sensory methods may be considered costly and not always practical for large-scale commercial purposes.

Rheological Methods

Rheological techniques are one of the most important methods used for the evaluation of the quality of fish and other seafoods. Texture is a very important quality parameter and is of interest to producers, processors, and consumers. Alongside with the development of sensory evaluation (discussed in the sensory analysis section), many instrumental methods have been developed for measuring the textural properties of fish and other seafoods.

In a pioneering review related to mechanical/physical methods most commonly cited in the literature to determine rheological properties of frozen fish samples, Barroso et al. (1998a) reported that the heterogeneity of fish structure and variety of products that exist (such as fillets, whole fish, mince) causes problems with sample preparation which must be taken into

consideration when choosing methods (Kramer test, Warner-Bratzler procedure, puncture test, compression methods, tension analysis, and so on) for assessing fish quality. The authors suggested the use of more than one method to establish fish quality.

Several studies attempted to classify fish and other seafood products into several quality categories according to their Kramer, Warner Bratzler, puncture test parameters, and time-temperature conditions (Barroso et al., 1998b; Nunak and Schleining, 2011). Based on several rheological parameters (viscosity, maximum force from Kramer, and energy from the puncture test) and multivariate statistical analyses, frozen hake fillets were classified into 4 quality categories ranging from excellent (low texture, high viscosity) to very poor (high texture, low viscosity) quality (Barroso et al., 1998b). In order to identify the most suitable method to be used to evaluate texture changes of raw white shrimp, during storage in ice for up to 14 days, Nunak and Schleining, (2011) investigated different methods (relaxation, compression, texture profile analysis, cutting, and penetration tests) at different speeds (0.1, 0.5, and 1.0 mm/s) and positions (second, third, and fourth segments of abdominal musculature). The best results were obtained on the second flesh segment by using penetration as a parameter and a spherical probe at a speed of 0.1 mm/s. These results were in disagreement with those of Casas et al. (2006) who measured the textural characterizations of Atlantic salmon stored at 2 °C using diverse instrumental methods performed at 3 different positions along the fillet (tail, back, and belly regions). The tail region was found to be the firmest one. The compression test with a cylindrical probe was found to be the most appropriate one, allowing the discrimination between the 3 different regions. One of the main conclusions of this study was that texture measurement must be taken at the same fish location.

Numerous other mechanical methods have been used to measure texture of fish and other seafoods; nevertheless, there is a little agreement on which is the best method (Cheng et al., 2014). Coppes-Petricorena (2011) summarized various instrumental methods commonly used for determining texture, and indicated that most research studies were carried out using a TA.XT2 texture analyzer. By using this instrument, it was found that: i) hardness of smoked salmon muscle increased and its elasticity decreased, with increasing brine concentration (Gallart-Jornet et al., 2007); and ii) freezing salmon samples during 24 hours before smoking induced a negative effect on the adhesiveness and cohesiveness of the flesh (Martinez et al., 2010). In another study, textural properties of ray fish muscle were measured using the Warner-Bratzler shear force method in a universal testing machine with a speed of 3 mm/s during storage in ice for 18 days (Ocaño-Higuera et al., 2011). With increasing storage time, the authors pointed out a significant decrease in force necessary to shear the muscle passing from 16.18 kgf in fresh fillets to 5.60 kgf after 18 days storage in ice.

Other textural parameters; compression and penetration tests, were applied using a TA-Hdi texture analyzer equipped with flat-ended cylindrical probe to investigate the textural properties of Indian Rohu fish during storage in ice for 8 days (Jain et al., 2007). A significant decrease in skin hardness and stiffness, varying from 95.8 to 48.7 N and from 4.63 to 2.0 N/mm, was observed during the storage period, respectively. One of the main conclusions of this study was that the development of a modified Maxwell model capable of prediction of the fish skin hardness with an error of 0.06%.

Some authors were interested in studying changes in fish muscle in terms of texture and structure during postmortem storage and the impact of different handling and processing methods such as

smoking, freezing–thawing treatments, and so on (Ayala et al., 2010; Cheng et al., 2014; Sigurgisladottir et al., 2000). Structural changes of sea bream fillet, measured with transmission electron microscopy, exhibited a detachment among fibers up to 5–10 days postmortem as a result of a rapid proteolysis in the muscle tissue, then a loss of I-band, Z line, and actin filaments were observed (Ayala et al., 2010). In the same research study, texture measurements were carried out through an empirical technique, namely texture profile analysis using a two-cycle compression test, which was measured in a QTS-25 texturometer. The results indicated that, except for springiness, all parameters decreased within 5 days of storage, in particular hardness, gumminess, and chewiness which decreased sharply by about one-half, in comparison with values observed at prerigor. In a similar investigation, Sigurgisladottir et al. (2000) monitored changes in microstructure and texture during smoking of fresh and frozen salmon originating from Iceland and northern and western Norway (60 specimens from each origin). The authors used light microscopy to examine changes in fillets in terms of diameter, cross-sectional area, and number of fibers, while the TA.XT2 texture analyzer was utilized to measure forces required to shear salmon fillets. It was found that the frozen–thawed fish muscle fibers became shrunken, the extracellular space became larger, and the force was lower compared to the fresh samples. Concerning smoking effect, the space between the fibers and the fiber shrinkage increased to a higher degree in salmon muscle submitted to freezing before smoking. Additionally, smoking effect on shear force differed according to smoking conditions and fish origin.

Many attempts have been made to establish a correlation between the texture of fish and seafoods measured by instrumental methods and sensory analysis, but varying results have been reported. However, only few studies have found a relationship between the 2 methods due to the

very heterogeneous-making sampling (Hyldig and Nielsen, 2007). For example, Schubring, (2002) demonstrated a relatively high correlation (R = 0.84) between sensory assessment and textural measurements of unfrozen cod stored in melting ice, allowing the authors to recommend the use of a hand-held device to determine fish texture due to its speed and low cost. In another study (Mørkøre and Einen, 2003), sensory analysis measurements of raw and smoked Atlantic salmon were compared with those of a texture analyzer equipped with 4 different probes: 12.5 and 23 mm cylinders, a Warner-Bratzler blade, and a 25.4 mm sphere. Results showed that hardness of raw fish determined by cylindrical probes was found to be the best method to be correlated with sensory analysis (R = 0.65).

Some studies have been performed to assess the potential of instrumental measurements to authenticate fish samples. In a study conducted by Alasalvar et al. (2002), differentiation between wild and farmed fish samples was recognized by using a flat-ended cylinder, simulating the human finger. The authors noticed that, starting day 16 of storage, the wild sea bream was found to be significantly softer than the cultured one.

Besides the texture, viscosity is one of the most sensitive functional properties for measuring changes occurring during frozen storage of fish (Barroso et al., 1998a). Therefore, measurement of fish muscle viscosity could be proposed as an indicator of fish quality. The effect of ice storage on the physicochemical and dynamic viscoelastic properties of ribbonfish meat was evaluated in a study by Dileep et al. (2005). An increase in the viscosity was observed after 10 days of ice storage, indicating a change in protein conformation. This was confirmed later by Geirsdottir et al. (2007) who also observed an increase of viscosity of whole muscle Icelandic herring at pH = 2.7 after 3 months of frozen storage, while at pH = 11 a significant increase was

observed after 1 week compared to fresh herring fillets. These changes in viscosity were attributed to the reduction in protein solubility and an increase in lipid oxidation. According to the authors, modifications in the viscosity indicated that frozen storage affected the structural and functional properties of the muscle proteins.

The instrumental methods used for the evaluation of rheological parameters allow getting more objective and reliable measurements of textural properties compared to sensory ones. In addition, texture measurements with instrumental methods: i) avoid the high costs of highly trained personnel; ii) are highly repeatable; and iii) most of all, do not suffer from fatigue or adaptation as sensory evaluation could do. However, as stated above, the heterogeneity and the complex structure of fish and other seafoods could impose some restrictions to the use of specific textural instruments. Moreover, the segmentation and orientation of the fillet structure makes it difficult to prepare samples of a standard size and dimension.

Electrical Measurements

Electric properties (resistance, conductivity, and capacitance) of fish flesh determined by Torrymeter and Fischtester have been used to evaluate freshness of fish and other seafoods. The technique is based on the measurements of the resistance and conductivity of fishes. Fresh samples presented resistance and conductivity of 2000 Ω and 500 μS, respectively, whereas the spoiled ones presented values of 50 Ω and 20,000 μS for respectively. This is due to disruption of the cell membranes by autolytic spoilage, and later by microbial action, causing leaking of cell fluid into the intercellular space, and leading to a decrease in electrical resistance and capacity (Oehlenschlager, 2014).

. Lougovois et al. (2003) compared several methods (e.g., sensory, K value, microbiological, and Torrymeter measurements), for assessing freshness and remaining storage life of gilthead sea bream stored in ice. Torrymeter values were found to decrease in a linear manner (R^2 = 0.96) during the storage, allowing the authors to claim that this technique provided a fast and reliable tool to determine fish freshness, with an accuracy of ± 2.2 days. This result was in accordance with the investigations of Oehlenschlager (2005), who used a Fischtester to determine the freshness of several fish species. As for Torrymeter, the author reported a linear decrease of Fischtester readings throughout the whole storage period. High correlation (R= −0.96) between Fischtester results and QIM scores was observed.

When freezing, storage, and thawing are done properly, the sensory properties of the fish and other seafood products are very similar to those of the fresh ones. Consequently, it is difficult to differentiate between fresh from frozen–thawed fishes. This was explained by the similarity of physical and chemical characteristics of fresh and frozen-thawed fishes (Duflos et al., 2002; Karoui et al., 2006a). However, a comparison between enzymatic measurements and Torrymeter readings of plaice, whiting, and mackerel, demonstrated the reliability of the Torrymeter to discriminate fresh from frozen–thawed fish samples (Duflos et al., 2002). Indeed, the authors observed a steady decline of Torrymeter values as spoilage progressed, which had similar effects to freezing. One of the main conclusions reached by the authors was that Torrymeter could be used for a reliable differentiation between frozen–thawed and fresh whole fish.

Although the importance of the electrical measurements by Torrymeter and Fischtester for fish freshness evaluation, there are several factors that may affect the results. Mechanical abuse, such as the loss of skin and damage caused by bruising or rough handling during harvesting and

packing operations, could result in more variable values. In addition, fish stored in sea-water and high salt content in water-ice may give erroneous results.

Spectroscopic Techniques Used for Quality Determination of Fish and Other Seafoods

Although the importance of the traditional techniques is unquestionable, they are hardly possible to implement for rapid practical use when many samples need to be analyzed on-line or at-line in the food industry. Moreover, these methods are also time-consuming and susceptible to large variations (temperature, pH, and so on). Spectroscopy in the ultraviolet (UV), visible (VIS), and infrared (IR) regions of the electromagnetic spectrum is becoming more and more attractive analytical technique for measuring quality parameters in food with decreasing instrument prices, improved equipment, and chemometric tools. Other spectroscopic techniques such as NMR and Raman spectroscopy have also been successfully applied in diverse fields of both food research and manufacturing. The main advantages of using spectroscopic techniques are rapid data acquisition, the possibility of simultaneous determination of several quality parameters, and the ability to replace expensive and time-consuming reference techniques (Cozzolino and Murray, 2012; Karoui et al., 2010; Karoui and Blecker, 2011; Liu et al., 2013)

In recent years, qualitative and quantitative applications of the spectroscopic techniques have been developed in the fish sector. These applications include: (i) evaluation of fish freshness; (ii) relevant authenticity issues of fish which concern species, geographical origin, and production method (wild/farmed, fresh/frozen-thawed); (iii) detection of microbial behavior and spoilage; and (iv) prediction of some physicochemical and textural parameters.

Fluorescence Spectroscopy

Fluorescence spectroscopy is a rapid and nondestructive technique allowing the screening of a large number of different food products (Karoui and Blecker, 2011). This technique has been widely used in biological sciences due to its high sensitivity and specificity (Christensen et al., 2006). Fluorescence is the emission of light subsequent to absorption of UV or VIS light of a fluorescent molecule or substructure, called fluorophore. Thus, the fluorophore absorbs energy in the form of light at a specific wavelength and liberates it in the form of emission of light at a higher wavelength.

In conventional fluorescence spectroscopy, 2 basic types of spectra are usually measured: (i) when a sample is excited at a fixed wavelength λ_{ex}, an emission spectrum is produced by recording the emission intensity as a function of the emission wavelength λ_{em}; and (ii) an excitation spectrum may be obtained when λ_{ex} is scanned while the observation is conducted at a fixed λ_{em}. In food analysis, the emission spectra at a particular λ_{ex} are typically studied. Recently, synchronous fluorescence spectroscopy (SFS) has shown great potential in many applications. For this technique, the excitation and emission wavelengths vary simultaneously keeping a positive difference ($\Delta\lambda$) between the 2 wavelengths ($\Delta\lambda = \lambda_{em} - \lambda_{ex}$). The SFS allows the consideration of the whole fluorescence landscape (spectra recorded at different offsets), and retains information related to several fluorophores compared to a classical emission or excitation spectrum, which is mainly specific to a sole fluorophore.

When a set of emission spectra at different λ_{ex} is recorded, a three-dimensional landscape is obtained. This fluorescence landscape (EEM) enables us to obtain more information about the fluorescent species present in the sample, because the bands arising in the wider axes are

considered (Sadecka and Tothova, 2007). Although EEM spectroscopy has been widely used for quality control in many foods, only very few studies can be found in the literature for the quality assessment of fish and other seafoods (Eaton et al., 2012).

For further information on the principle of fluorescence spectroscopy, the reader may refer to other sources (Christensen et al., 2006; Karoui and Blecker, 2011; Sadecka and Tothova, 2007). Therefore, this section will only focus on applications of fluorescence spectroscopy for determining quality of fish and other seafood.

Fish and other seafoods contain several intrinsic fluorophores, including aromatic amino acids and nucleic acids (AAA+NA), tryptophan, tyrosine, and phenylalanine in proteins; vitamins A and B_2; nicotinamide adenine dinucleotide (NADH), and numerous other compounds that can be found at low or very low concentrations. Thus, fluorescence studies on fish and other seafoods reported in the literature are dominated by fluorescence assigned to tryptophan, NADH, vitamin A, and fluorescent oxidation products.

As mentioned above, the lipid fraction of fish and other seafoods contains high levels of polyunsaturated fatty acids. During processing and/or storage, the degradation of polyunsaturated fatty acids leads to the development of primary and secondary products, resulting in the formation of fluorescent compounds and the loss of nutritional quality. Several studies have measured the fluorescent properties of fish at different excitation/ emission maxima, and 2 of these ratio maxima (393/463 and 327/415 nm) showed a high correlation with the formation of oxidation products of fish samples. Since lipid oxidation induces a fluorescence shift toward higher wavelength maxima, fluorescence ratio, defined as the fluorescence intensity at 393/463 over that at 327/415 nm, has been used as an indicator of rancidity development during frozen

storage of many fish species. Aubourg et al. (1998) used the fluorescence ratio to monitor changes occurring in fatty fish (sardines) stored at −18 °C up to 24 months, and those stored at −10 °C up to 120 days. This ratio, determined in the aqueous solution, was found to increase throughout the entire period, regardless of storage temperature. These results were confirmed later by the same authors (Aubourg and Medina, 1999) on 2 lean fish species (cod and haddock), demonstrating that fluorescence detection was sensitive for assessing fish freshness during chilling of lean and fatty fish species. However, although the fluorescence shift was found to be a more effective index of fish quality than other commonly used indicators (such as TVB-N), the use of only emission or excitation maximum wavelength could induce some loss of information that could be contained in fish samples.

With classical right-angle fluorescence spectroscopy, the measurements are carried out in dilute solutions where the absorbance is below 0.1. At a higher absorbance rate, a decrease in fluorescence intensity and a distortion of emission spectra are observed due to the inner filter effect. To overcome such problems, front face fluorescence spectroscopy (FFFS) was developed where only the surface of the material is illuminated and examined. The emitted photons are collected at an angle of 56° to the surface of the sample, to minimize artifacts generated by the photons of excitation reflected from the sample. This technique allows a quantitative investigation of fluorophores in powders as well as in concentrated or even opaque samples. In this context, excitation wavelength set at 382 nm was used to record spectra in the 450–750 nm region on 4 different batches of salmon pâté stored at 4 °C for 4, 8, and 13 weeks (Olsen et al., 2006). Citric acid or calcium disodium ethylenediamine tetra-acetate was added as metal chelators to 2 batches, whereas no chelator was added to the third one. The 3 investigated

batches contained oil, while the fourth one contained the same amount of ingredients without oil. By applying the PCA approach to the collection spectral data sets, a clear difference between samples according to storage time was observed; the largest variation in the data sets was attributed to whether the sample contained oil or not. In a second step, the authors attempted to predict the age of salmon by applying PLSR. The correlation coefficients between physicochemical properties and sensory, dynamic head-space, fluorescence, and electronic nose measurements were 0.64, 0.94, 0.93, and 0.70, respectively. The corresponding root-mean-square errors of prediction were 3.8, 1.7, 1.8, and 3.5, respectively, illustrating that the FFFS could be a suitable technique to measure lipid oxidation in fish samples. This was confirmed by the high correlation value ($R > 0.8$) found between fluorescence spectra and sensory attributes. The obtained results were confirmed later in a study by Airado-Rodriguez et al. (2010) who monitored the oxidation of cod caviar paste samples stored at 4 °C with the presence of O_2, N_2, and with or without the presence of light after excitation set at 382 nm. The authors observed a broad and intense peak in the 410-500 nm region, especially for samples exposed to light, which were ascribed to products formed by the reaction of unsaturated aldehydes with proteins, while the peak at about 470 nm was attributed to oxidation products.

Reported studies on the use of the FFFS as a method for monitoring fish freshness are scarce (Dufour et al., 2003; Karoui et al., 2006a). The AAA+NA, tryptophan, and NADH spectra recorded on 4 fishes species (cod, mackerel, salmon, and whiting fillets) kept in ice for 1, 5, 8, and 13 day(s) were scanned after excitation at 250, 290, and 336 nm, respectively (Dufour et al., 2003). The spectra of the first 2 excitation wavelengths showed maxima located at 338 and 336 nm, respectively, while the last excitation wavelength (336 nm) exhibited two maxima at 414

and 438 nm. For the 3 excitation wavelengths examined in this study, the shape of the spectra illustrated some differences according to storage time. Applying FDA to the tryptophan fluorescence spectra allowed only 56% of samples to be correctly classified, indicating that tryptophan spectra failed to monitor fish freshness. Better classification was obtained from AAA+NA and NADH, since 92% and 74% of correct classification were observed, respectively. One of the main conclusions of this study was that the AAA+NA fluorescence spectra could be considered as fingerprints that may allow discrimination between fresh and aged fish fillets. The obtained results were confirmed recently (Hassoun and Karoui, 2015) on whiting fish samples stored under different refrigerated conditions (presence/absence of light, partial/total vacuum). The same research group (Karoui et al., 2006a) has assessed the potentiality of FFFS to differentiate between fresh and frozen-thawed fish samples. A total of 24 fish (12 fresh and 12 frozen-thawed) were analyzed by using excitation wavelengths set at 290 (tryptophan) and 340 nm (NADH). The emission spectra of NADH of fresh fish samples showed a maximum at 455 nm and a shoulder at 403 nm, while frozen-thawed fish samples were characterized by a maximum located at 379 nm and a shoulder at 455 nm (**Figure 1**). By applying PCA to the normalized NADH spectra, a clear discrimination between fresh and frozen fish samples was observed, which was confirmed by the FDA model, since complete (100% and 100%) correct classifications were obtained for the calibration and validation data sets, respectively **(Figure 2**). One of the main conclusions of this research was that the NADH fluorescence spectra may be considered as a promising tool for differentiating between fresh and frozen-thawed fish samples.

Although SFS has shown its utility in many different food applications, there are few papers discussing the use of this technique for fish and other seafoods. Recently, SFS was used for

measuring pyrene concentrations in the gills of carp fish (Liu et al., 2012). The Δλ between excitation and emission wavelengths was maintained at 50 nm and the measurements were conducted in the 280-450 nm spectral range. The excitation and emission maximum peaks appeared at 334.5 and 384.5 nm, respectively. In addition, a high correlation was observed between pyrene concentrations (1–1000 μg L^{-1}) in n-hexane solution and fluorescence intensity, since R of 0.99 was obtained. These results indicated the potential use of SFS as a technique allowing to determine pyrene levels in fish samples.

As mentioned above, only few studies were found in the literature on the application of EEM spectroscopy for fish and other seafood products. One of the rare studies on the use of EEM for quality assessment of seafoods was that of Eaton et al. (2012) who investigated the potential of this technique in the range of 230-600 nm and 240-600 nm for excitation and emission, respectively, to classify 2 species of shrimp collected from 4 different countries (Ecuador, Philippines, Thailand, and the USA). Although a small number of samples (six samples from each location) were tested, the authors succeeded, by applying PARAFAC and SIMCA approaches, in correctly identifying the country of origin for 95% of the samples. Such a finding allowed the authors to conclude that fluorescence spectroscopy permits to classify fish samples according to their geographical origins.

The principal advantages of fluorescence spectroscopy are its rapidity and specificity since this technique is considered to be 100–1000 times more sensitive than other spectrophotometric techniques. In addition, fluorescent compounds are extremely sensitive to their environments at the molecular level. Hence, fluorescence spectroscopy can be used as an accurate tool for monitoring the molecular changes occurring during handling, processing, or storing of fish and

other seafoods. However, the major disadvantage of fluorescence is its strong dependence of light scatter and environmental factors such as temperature, pH, viscosity, and sample color. Moreover, the interaction between a fluorophore and other substances present in the system could induce quenching phenomena, resulting in the reduction of fluorescence intensity as well as changes in the shape of the spectra.

Infrared Spectroscopy

In the last few years, infrared (IR) spectroscopy has become one of the most attractive and commonly used methods of analysis for simultaneous, rapid, and nondestructive determination of major components in many agriculture-related products and plant materials. Chemical bonds present in the organic matrix of fish and other seafoods vibrate at specific frequencies, which are determined by the mass of the constituent atoms, the shape of the molecule, the stiffness of the bonds, and the periods of the associated vibrational coupling. Recent advances have allowed infrared technology to be extended further by development of Fourier transform infrared (FTIR) spectroscopy. In addition, the use of attenuated total reflectance (ATR) with FTIR allowed the spectral collection from solids, liquids, semisolids, and thin films. ATR IR spectroscopy provides a fast analytical tool as compared with traditional IR transmission spectroscopy, requiring less sample preparation, improving sample-to-sample reproducibility, and minimizing user-to-user spectral variation (Cheng et al., 2013b; Cozzolino and Murray, 2012; Karoui et al., 2010; Liu et al., 2013; Nilsen and Heia, 2009; Stuart, 2004).

The infrared radiations of the electromagnetic spectrum are divided into 3 regions: near, mid, and far infrared. The far-infrared region is at approximately 400–10 cm^{-1}, lying adjacent to the

microwave region, while mid-infrared (MIR) and near-infrared (NIR) regions are at 4000–400 cm^{-1} and 4000-14000 cm^{-1}, respectively.

Most literature references related to IR spectroscopy report the use of this technique to: i) determine fish freshness; ii) predict chemical composition; and iii) identify fish and other seafoods.

Near-Infrared Spectroscopy

As NIR spectra are, for the most part, the result of overtone bands of fundamental groups containing C–H, O–H, and N–H bonds, organic molecules may be investigated by using this approach (Stuart, 2004). The operating principle of the measurement of this technique is based on sending light onto the sample and then measuring the light coming from the sample at different wavelengths. When the light is sent through the sample, it is named 'transmission' or 'transmittance' measurement. When the illumination and detector unit is located on the same side of the sample, the measurement is referred to as 'reflection' or 'reflectance'. A 'transflection/transflectance' measurement, also called 'diffuse reflectance', refers to the situation when the sample is illuminated and measured on the same side, but not in the same location (Nilsen and Heia, 2009; Stuart, 2004).

NIR spectroscopy has established itself as a useful analytical technique in the food industry with data mining and data processing based on chemometric tools. The recent advances in the evaluation of fish quality using NIR spectroscopy have been reviewed in several publications (Cozzolino and Murray, 2012; Liu et al., 2013; Pu et al., 2015). Indeed, the technique has been successfully used to predict several fish quality attributes and to authenticate fish and other

seafoods. The main research activity in the NIR spectroscopy has concerned the assessment of freshness, chemical, and microbiological parameters of fish and other seafoods (Liu et al., 2013). One example of application of NIR spectroscopy to evaluate freshness of seafoods was the study of Madigan et al. (2013), in which this technique was investigated in the reflectance mode, covering the NIR region between 833 and 2630 nm, to characterize changes in freshness of half-shell Pacific oysters stored at 4 °C for 5 days. In this study, the storage time (R^2= 0.8, and ratio of the error range = 5.37) and the odor of oysters (R^2 = 0.77 and ratio of the error range =7.77) rather than their color, were successfully predicted using NIR spectroscopy and chemometrics.

Spectroscopy in visible and near-infrared (VIS/NIR) regions has received much attention due to the fact that most of the agro-food products contain functional groups like C–H, N–H, and O–H, which are closely associated with the overtone and combination vibrations in the VIS/NIR spectral region (Pu et al., 2015). The technique has also been applied to the determination of fish freshness. For instance, the potential of this technique in the 400-1100 region nm to monitor cod and salmon freshness during 2 weeks of storage in ice was investigated (Nilsen et al., 2002). The correlation between spectral data and storage time was modeled by PLSR, and the authors observed that the VIS region retained the most useful freshness information for the cod with prediction correlation and an error value of, respectively, 0.97 and 1.04 days. For the salmon, similar results were obtained with the NIR region since prediction correlation and error value of 0.98 and 1.20 days were obtained, respectively. This study illustrated that NIR spectroscopy could enable rapid, nondestructive, and low-cost measurements for the evaluation of fish freshness.

Spoilage in fish and other seafoods is a major potential health hazard and could cause significant economic loss to the industry sector. Organoleptic characteristics associated with spoilage can include changes in appearance (such as discoloration), development of off-odors, slime formation, and so on, that make fish products undesirable for human consumption. It is widely accepted that detectable organoleptic spoilage is a result of decomposition and the formation of metabolites caused by the growth of microorganisms. In this context, several studies have been conducted to detect microbiologically spoiled or contaminated fish products. For example, the potential of NIR spectroscopy in the 800-2500 nm region to predict bacterial counts in salmon stored for up to 9 days at 4 °C was explored (Tito et al., 2012). PLSR models were developed on 72 data points and total aerobic plate counts were predicted with R^2 values of 0.95 and 0.64, respectively, for the calibration and validation data sets. One of the main conclusions of this study was that, although further model development is required, NIR spectroscopy could be used to predict bacterial numbers and, thus, shelf-life of Atlantic salmon and other seafood, in agreement with the findings of Lin et al. (2006) who succeeded in detecting spoilage and quantifying microbial loads of rainbow trout in the 600-1100 nm region. The authors used: i) minced samples stored at 21 °C and acquired spectra at 0, 2, 4, 6, 8,10, 12, and 24 hours; and ii) intact fillet samples stored at 4 °C and sampled daily for a period of 8 days. By applying PCA to the spectral collection, the authors noted a clear differentiation between samples stored at 4 °C and aged 1 day from those aged 4 days or more. Similar results were obtained from rainbow trout kept at 21 °C since a clear segregation was observed between control samples (0 hour) and those of 10 hours or more. In a second step, the authors applied PLSR to predict microbial load, and the best results were obtained by transflection measurements on intact fillet, giving R values of

0.94 and 0.97 and error prediction values of 0.53 and 0.38 log cfu/g for skin and flesh sides, respectively. The authors concluded that NIR spectroscopy coupled with chemometric tools could be considered as a powerful tool to detect and monitor the spoilage process in rainbow trout in a rapid and nondestructive way.

Several studies have been performed to assess the potential of NIR spectroscopy to authenticate fish and other seafoods. For example, Ottavian et al. (2012) succeeded in differentiating between wild and farmed European sea bass samples. By applying a series of statistical analyses such as PCA and PLS-DA, the authors indicated that CH, CH_2, CH_3, and H_2O groups, which are related to fat, fatty acids, and water content, were the most interesting spectral regions. Another application related to authentication issues of red sea bream was performed by Uddin et al. (2005) who attempted to determine whether VIS/NIR spectroscopy in a reflection mode could differentiate fresh fish samples from frozen-thawed ones. PCA was applied to 108 samples (54 were used soon after arrival, while the second lot of 54 fish was kept at −40 °C for 30 days), and a clear discrimination of frozen-thawed samples from the fresh ones was observed. This difference has been attributed to the fact that the freeze-thawing treatment altered the physical structure of at least the surface layer of frozen-thawed fish, inducing changes in the shape of spectra. The authors claimed the use of VIS/NIR spectroscopy as a rapid tool for online or at-line processing control of fresh and frozen/thawed fish samples.

In the past decade, a new technique, referred to as imaging spectroscopy, has been developed in the VIS/NIR region, namely hyperspectral imaging (HSI). In addition to the spectral information, this technique also gives spatial information, which means that a full spectrum is recorded at different locations of the fish sample. Recently, the differentiation between fresh, fast frozen-

thawed and slow frozen-thawed fish samples has been achieved using a pushbroom HSI system in the 380-1030 nm region (Zhu et al., 2012). The authors observed differences in the shape of the spectra and ascribed them to the: i) alterations of physical structure, at least in the surface layer of fish; and ii) biochemical and textural changes in fish during freezing and frozen-thawed operations. By applying the SVM approach to the spectral and textural variables, correct classification rate of 97.2% was observed, indicating that HSI could be used as an on-line technique for rapid and nondestructive differentiation of fresh and frozen-thawed fish samples. These results confirmed previous findings by Sivertsen et al. (2011) who succeeded in differentiating between fresh and frozen-thawed cod fishes using the same technique. The most change was found around 507 and 636 nm and was ascribed to the oxidation of hemoglobin and myoglobin. Additionally, sampling was found to present a major impact on the sample freshness since the best spectral region for freshness prediction was located in the tail region and in the loin and neck area of the fillet. For more information about applications of HSI for seafoods and other food products readers can refer to interesting detailed reviews (Cheng and Sun, 2014; Dai et al., 2014; Pu et al., 2015) published recently in this field.

Reported studies on the use of NIR spectroscopy to predict some chemical parameters in fish and other seafoods have been published (ElMasry and Wold, 2008; Khodabux et al., 2007; Xiccato et al., 2004). Good predictions of chemical parameters, namely, moisture, protein, total fat, and free fat from NIR spectroscopy in the 600–2500 nm region were obtained from 38 tuna fishes, since R^2 values of, respectively, 0.98, 0.99, 0.95 and 0.96 were observed (Khodabux et al., 2007). These results were later confirmed by ElMasry and Wold, (2008) who succeeded in predicting fat and moisture contents in fillet of different fish species (Atlantic halibut, catfish, cod, mackerel,

herring, and saithe) by using the VIS/NIR region at 460 - 1040 nm. Correlation coefficients of 0.94 and 0.91 with root mean square error of cross-validation (RMSECV) of 2.73% and 2.99% were obtained, respectively, for moisture and fat contents. According to these results, the authors concluded that NIR spectroscopy provides good reliability to predict the chemical compositions of sea bass fish.

In a similar approach, NIR spectroscopy was utilized to determine proximate chemical composition of European sea bass located in 3 Italian regions and sourced from different rearing systems (extensive ponds, semi-intensive ponds, intensive concrete tanks, and intensive sea-cages) (Xiccato et al., 2004). The application of PLSR between reference methods and NIR spectroscopy data gave satisfactory predictions. For example, fresh minced fillet gave a good reliability for the prediction of: i) water (R^2 = 0.95 in both calibration and full cross-validation data sets, standard errors of calibration (SEC) = 0.85, and standard errors of cross-validation (SECV) = 0.87); ii) ether extract (R^2 = 0.97, SEC = 0.68, and SECV = 0.70); and iii) energy (R^2 = 0.96, SEC = 0.26 and SECV = 0.28). However, NIR spectroscopy failed to predict with good accuracy crude protein since R^2 of only 0.61 and 0.30 for calibration and full cross-validation data sets was observed, respectively. Sampling was found to have a huge impact on the accuracy estimation of chemical components by NIR spectroscopy since chemical composition of minced samples was found to be more accurately predicted by NIR spectroscopy than that of intact fillet, most likely because intact muscle absorbs more energy and, therefore, provides less reflectance compared to homogeneous minced fillets.

On the basis of the studies mentioned above, it could be concluded that VIS/NIR spectroscopy is a valuable and useful analytical technique that could be applied for the rapid assessment of fish

quality and authenticity. In addition, this versatile technique provides extensive information on fish quality, allowing simultaneous identification of quantitative and qualitative changes of various chemical components (proteins, fat, water) involved in loss of fish quality during handling, processing, and storage. Nevertheless, there are some limitations concerning the applications of this technique since it failed to predict sensory attributes of fish, mainly due to the highly heterogeneous nature of fish samples and the low precision and subjectivity of the reference method. Another disadvantage of this technique is the complexity of NIR spectra, and the need to develop calibration models based on the use of chemometrics to predict unknown samples. On the other hand, the success of NIR spectroscopy depends on the reliability of the reference method employed and the sample presentation (Garrigues and Guardia, 2013; Liu et al., 2013).

Mid-Infrared Spectroscopy

The MIR region of the electromagnetic spectrum lies between 4000 and 400 cm^{-1} and can be segmented into 4 broad regions; the X-H stretching region (4000-2500 cm^{-1}), the triple bond region (2500-2000 cm^{-1}), the double bond region (2000-1500 cm^{-1}), and the fingerprint region (1500-400 cm^{-1}) (Karoui et al., 2010; Stuart, 2004). MIR spectroscopy is the most informative part of the infrared spectrum and may be used to study the fundamental vibrations and associated rotational-vibrational structure. However, research studies involving the use of MIR spectroscopy to characterize quality of fish and other seafoods are relatively limited (Karoui et al. 2010).

The use of Fourier transform mid-infrared (FT-MIR) spectrometers has significantly increased the capabilities and applications of MIR spectroscopy. This recent technique has replaced dispersive spectrometers because of their higher speed and sensitivity; all frequencies are examined simultaneously. In this context, Karoui et al. (2007a) used FT-MIR to differentiate between fresh and frozen-thawed fish samples. A large difference between frozen–thawed (n=12) and fresh (n=12) fish spectra was observed throughout the 1700–1500 cm^{-1} spectral region (**Figure 3)**. Regarding the 1500-900 cm^{-1} spectral region, fresh fish samples exhibited 2 peaks located at 1338 and 1419 cm^{-1} which were not present in the frozen-thawed ones. Moreover, fresh fish samples showed the lowest intensity in the 1200–900 cm^{-1} region, on the contrary to frozen-thawed fish samples. By applying FDA to the normalized spectral data in the 1500-900 cm^{-1}, 100% and 75% of correct classification were obtained for the calibration and validation data sets, respectively. Better classification was obtained using the 3000–2800 cm^{-1} spectral regions with correct classification rates of 100% and 87.5% for the calibration and validation data sets, respectively. One of the main conclusions of this study was that the FT-MIR spectroscopy, particularly the 3000–2800 cm^{-1} spectral region, could be a useful tool to differentiate frozen–thawed fish samples from fresh ones.

Reported studies on the use of FT-MIR spectroscopy as a method for determining physicochemical parameters in fish and other seafoods are limited. Recently, a research study (Hernández-Martínez et al., 2013) assessed the potential of FT-MIR in reflectance mode to predict total fat, fatty acids, content of omega-3, and fish lipid quality index of 3 fish species (Atlantic bluefin tuna, crevalle jack, and Atlantic Spanish mackerel). Fillets from these different species (28 samples of each one) were kept under refrigeration at 0-0.5 °C for up to 13 days and

then characterized chemically and spectrophotometrically at 4 different season captures (beginning and end of summer, beginning and end of autumn) and storage times (0, 2, 5, 7, 9, 12, and 13 storage day). By applying PLS, the authors obtained a good reliability for the prediction of total fat (R^2 = 0.97, Residual Predictive Deviation of cross-validation RPDcv = 4.76), fatty acids ($0.89<R^2<0.99$, $2.35<RPDcv<7.68$), fish lipid quality index (R^2 = 0.99, RPDcv = 8.52), and omega-3 (R^2 = 0.97, RPDcv = 3.74). These results allowed the authors to conclude that this technique along with an appropriate chemometric tool could provide rapid and accurate results with neither sample preparation nor toxic waste. More recently, the same research group (Hernández-Martínez et al., 2014) used the same technique for the prediction of other quality parameters (chemical composition, pH, TVB-N, TBARS, and PV) on the aforementioned species (Atlantic bluefin tuna, crevalle jack, and Atlantic Spanish mackerel). Again, the authors applied PLS on FT-MIR spectra and good prediction was obtained for chemical composition ($0.97<R^2<0.99$, $5.01<$ RPDcv $<5.59\%$), pH (R^2 = 0.987, RPDcv = 7.18%), and TVB-N and oxidation indices ($.94<R^2<0.97$, $3.21<$ RPDcv $<3.67\%$). The rapidity to obtain the results on a small amount of sample motivated the authors to recommend the use of FT-MIR technique for routine analysis in fish industries as an alternative for classical chemical methods.

With the aim of studying the oxidative stability of lipids and proteins in fish and other seafoods, some manufacturing processes such as smoking and salting were applied to accelerate the oxidation process. For example, under oxidative conditions, lipids extracted from salted and unsalted farmed salmon fillets showed a significant modification in the 3600-3200 cm^{-1} region (Guillen et al., 2004). The MIR spectra of unsalted salmon fillets submitted to oxidative conditions (50 °C in an oven with circulating air) remained practically unchanged for up to 17

days of storage. The authors attributed this trend to the fact that salmon fillets contain important proportions of carotenoids, which have antioxidant activity, thus inhibiting oxidation of the fish lipids. With regard to the salted fish, changes in the shape of spectra were observed after 2 days of storage, including in particular the broadening of the band at 3470 cm^{-1} and the diminishing of the band intensity values located at 3012 and 1746 cm^{-1}. Reduced oxidative stability of salmon fillet lipids by the salting process was ascribed by the authors to a probable loss of water-soluble antioxidants in fish fillets and/or to an increase of concentrations of pro-oxidant agents (Guillen et al., 2004).

Structural changes in protein during different handling and storage conditions could have an effect on fish quality, including modifications in the molecular mechanism of protein, structure reactions, and protein folding, unfolding, and misfolding. Thus, some relevant studies were conducted for predicting and monitoring the secondary structure of proteins by FT-MIR spectroscopy. As an example, FT-MIR micro-spectroscopy was used to investigate the changes in the myofibrillar proteins in salmon muscles due to dry-salting and smoking (Carton et al., 2009). It was shown that salting time mostly contributed to changes in the amide I region (1700-1600 cm^{-1}), indicating that secondary structural changes of proteins were primarily affected by salting, while the main variations in the amide II region (1600–1500 cm^{-1}) were provoked by smoking (Carton et al., 2009). These results were in agreement with the findings of Bocker et al. (2008) who used FT-MIR (4000-1000 cm^{-1}) microspectroscopy in a transmission mode to investigate the effects of brine-salting (16% NaCl) on the protein structure of Atlantic salmon muscle with respect to raw material variations (prerigor, postrigor, frozen/thawed). The highest salt uptake was achieved for frozen/thawed (4.1%), followed by postrigor (3.0%), and prerigor

(2.2%) salmons. Differences in the FT-MIR amide I spectral region related to changes occurring in the secondary structure of muscle were observed. Indeed, frozen/thawed salmon (4.1%) presented an increase in the band located at around 1668 cm^{-1} referring to an increase of nonhydrogenated C=O groups.

The use of MIR spectroscopy is characterized by high repeatability and very easy sampling. However, the disadvantage of this technique is its inability to measure molecules with very low concentrations. Moreover, in water-rich systems, like fish and other seafoods, the strong absorption of water due to the O–H bending band could obscure potentially useful absorption from protein.

Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy is one of the most commonly used techniques by both chemists and biochemists to identify molecular structures and to study the progress of chemical reactions. The NMR technique relies upon the fact that certain nuclei, most notably hydrogen, have the property of spin. The requirement is that nucleus has an odd number of: i) protons, ii) neutrons, or iii) protons and neutrons. The applications of NMR methods in food research can be divided into 3 main groups: magnetic resonance imaging (MRI), low-field NMR, and high-resolution NMR (Bekiroglu, 2011; Erikson et al., 2012).

During the past decade, high-resolution NMR has been utilized as a tool to assess the quality of fish and other seafoods. The main application of this technique concerns the authentication of marine oils and muscle lipids of both fatty and lean fish, according to production method (wild/farmed), geographical origin, species, and process history. As differences in both the

quality and price among fish species may lead to falsification and mislabeling, there is a need for a reliable method to trace their origins. In this regard, NMR spectroscopy is deeply rooted in the history of authenticity purposes in food sciences (Bekiroglu, 2011). Indeed, this technique has been employed to distinguish wild from farmed salmon samples since the former is often perceived by consumers as superior in terms of quality and nutritional properties compared to the latter. For example, Capuano et al. (2012) utilized ^{1}H NMR to differentiate between wild and farmed salmon regardless of their processing degree. By applying the SIMCA approach, complete classification (100%) of farmed and wild samples was achieved based on the fatty acid contents (oleic and linoleic acid contents). These results were in accordance with the findings of Vidal et al. (2012) who succeeded in discriminating between farmed and wild European sea bass due mainly to the high proportions of di-unsaturated acyl groups, mainly linoleic acid, in the farmed sea bass.

The lipid composition of farmed fish can vary greatly according to rearing condition, fish origin, and feeding system. In this regard, lipids extracted from Atlantic salmon muscle (n=195) originating from Norway, Scotland, Canada, Iceland, Ireland, the Faroes, and Tasmania were analyzed by ^{13}C-NMR (Aursand et al., 2009). By applying a series of multivariate statistical analyses, such as PNN and SVM techniques, correct classification rates of 98.5% and 100% were obtained, respectively, confirming previous findings of Masoum et al. (2007) who reported the ability of ^{1}H NMR to authenticate 141 salmon fish oils originating from 8 different areas (Canada, Alaska, the Faroes, Ireland, Iceland, Norway, Scotland, and Tasmania). The best discrimination of salmon fish was obtained when the authors used SVM, since correct classification of 95% was obtained, suggesting the application of this technique for

determination of the geographic origin. These results were later confirmed by Martinez et al. (2009) who attempted to classify Norwegian Atlantic salmon (n= 59) collected from 4 different farms by using ^{13}C-NMR coupled with gas chromatography (GC). By applying different chemometric tools (PCA, BBN, PNN, and SVM), SVM was found to be the best to discriminate between salmon samples, since 94.9% of correct classification was observed.

One of the most notable contributions of high-resolution NMR to food authentication concerns the determination of the isotopic content of a given fish species by using ^{13}C-NMR specific molecular sites. This technique, known as SNIF-NMR® for site-specific natural isotope fractionation, was applied to lipid fractions in order to determine the geographical origin, species, breeding stock, and wild/farmed origin of the fish. With regard to wild and farmed salmons (n = 38) caught in Norway and Scotland, 100% of correct classification was obtained following the application of canonical discriminant analysis (Aursand et al., 2000; Martinez et al., 2003).

Although the fatty acid composition of fish tissues varies according to season, age, diet, and environmental factors, genetic differences seemed to be the main factor to differentiate among fish species. This was evidenced by Standal et al. (2010) who utilized ^{13}C-NMR for lipid profiling, composed mainly of phospholipids, to authenticate 5 categories of lean gadoid fish (north-east arctic cod and Norwegian coastal cod, haddock, saithe, and pollack). By applying PCA, LDA, and BBN tools to the data sets, 100% correct classification of the 5 categories of fish was achieved using BBN.

Brix et al. (2009) conducted a study on the use of MRI to analyze seasonal variation in fat content and fat distribution in Atlantic mackerel using 17 fish samples at different nutritional

stages (starved and well fed), and the results were compared to triglyceride contents measured by GC. Globally, the authors succeeded in visualizing and quantifying fat contents of the investigated samples. However, only a slight correlation was observed between the fat content of the 2 methods (MRI and GC). The authors attributed this to the fact that the GC technique only picked up the triglycerides and not the other nonpolar fat classes determined by MRI.

Low-field NMR (LF-NMR) operates in a frequency range of 2-25 MHz and represents a simple and cheap version of traditional NMR methods. The technique has been proposed as a tool for analyzing muscle structure, including fat, water, and protein. In one application of this technique, Gudjónsdóttir et al. (2011a) attempted to determine the impact of polyphosphate concentrations and length of pre-brining and freezing on physicochemical properties of shrimp muscles using LF-NMR. Prior to cooking the shrimp at 80 °C for 15 seconds, 3 specific treatments were investigated using different sodium polyphosphate concentrations. The LF-NMR detected physicochemical changes, including protein, phosphate, and water contents as well as water-holding capacity, in shrimp muscle according to the concentration of sodium polyphosphate. The increased levels of polyphosphates during prebrining resulted in a reduction in protein denaturation and allowed, therefore, easy removal of the shrimp shell during cooking and freezing. Although an optimization process was still necessary with regards to measurement setting, number of samples, and size of analyzing surface, the authors suggested the use of LF-NMR for on-line or at-line quality control. This was supported by another investigation (Gudjónsdóttir et al., 2011b) which evaluated the effect of different pre-salting methods (brine injections with or without phosphates, brining, pickling, and kench salting) on the protein denaturation and changes in dry-salted cod fillet muscle properties. The authors pointed out a

high correlation between the NMR relaxation parameters and physicochemical parameters (moisture, salt, protein, and non-protein nitrogen content of the muscle, water-holding capacity, and pH). In additions, T1 and T2 values were found to be sensitive to detect protein denaturation. Indeed, brine injection followed by brining with low salt concentrations was found to induce less protein denaturation during the dry-salting and rehydration. From the obtained results, the authors suggested the use of LF-NMR for monitoring quality during the technological process. In another study (Sanchez-Alonso et al., 2012a), the authors used LF-NMR to monitor hake quality during storage at -10 °C for up to 6 months. A decrease and an increase in the amount of intramyofibrillar water and extramyofibrillar and extracellular water were observed, respectively. As storage time increased, a loss of juiciness and tougher texture were observed as a result of a decrease in the water-holding capacity and apparent viscosity values, together with an increase in the shear strength.

The NMR spectroscopic technique has several inherent advantages: the NMR instrument interacts with the investigated object by means of electromagnetic waves in the radiofrequency range. This makes most NMR techniques noninvasive and nondestructive, rapid, and nonpolluting for the environment. This method can be employed for rapid analyses of fat, water, and/or protein since the parameters present different relaxation times. In addition, NMR might be a better choice for analyzing heterogeneous samples such as fish and other seafoods. Thus, NMR applications in both fish industry and research could replace the traditional techniques progressively. However, the complex equipment of this technique and its low sensitivity compared to other spectroscopic techniques are the main disadvantages.

Raman Spectroscopy

Like MIR spectroscopy, Raman spectroscopy measures the fundamental molecular vibrations, but with different selection rules. By using this emission technique, the sample is irradiated with a monochromatic UV, VIS, or NIR beam generated by a laser, which allows the vibrational energy levels in the molecules to go from ground state to a state of high-energy collisions. When the molecule returns to a lower energy state, Raman scattering occurs with a lower frequency than the laser bream. Thus, quantitative and qualitative structural, as well as chemical, information of a given sample may be obtained simultaneously (Afseth et al., 2006). Although Raman spectroscopy has been successfully applied to detect adulteration as well as to differentiate foods according to their geographic origin, species, physicochemical properties, and process control, research studies involving the use of this technique to characterize quality of fish and other seafoods are limited.

Velioglu et al. (2015) proposed the use of Raman spectroscopy for the discrimination between fresh and frozen-thawed fish samples collected from 6 different species; horse mackerel (*Trachurus trachurus*), European anchovy (*Engraulis encrasicolus*), red mullet (*Mullus surmuletus*), bluefish (*Pomatamus saltatrix*), Atlantic salmon (*Salmo salar*), and flying gurnard (*Trigla lucerna*). After the application of PCA models, the authors observed that Raman spectroscopy could be a promising tool for a rapid discrimination of fish samples according to both their species and freshness (in terms of the number of freezing/thawing cycles). The technique was also applied to determine fat content and monitor lipid oxidation and protein structure in seafood products. Marquardt and Wold, (2004) used excitation laser set at 785 nm to determine the levels of carotenoid, collagen, and fat in different seafood products (cod, sea bass,

Pacific halibut, squid mantle, king salmon, and skate wing). Although no chemical reference measurement was performed in this study, the PCA approach applied to Raman spectra gave good information about fat, pigment, and collagen. In a similar approach, structural changes occurring in hake muscle proteins during frozen storage at -10 and -30 °C were investigated in a study by Herrero et al. (2004). The authors observed modifications in secondary structure of proteins mainly in the amide I (1600–1680 cm^{-1}) spectral region. Moreover, modifications in the tertiary structure were characterized by an intensity increase at the *v* C-H stretching band set at about 2935 cm^{-1}, indicating denaturation of the muscle proteins due to the exposure of aliphatic hydrophobic groups to the solvent.

The possibility of using Roman spectroscopy to identify structural changes of proteins and lipids during storage was confirmed later on both mackerel and horse mackerel kept at -80 °C overnight prior to freeze-drying and storage at 22 °C during 12 weeks (Sarkardei and Howell, 2007). A significant reduction in the protein extractability of the 2 fish samples during frozen storage was observed, indicating alterations of fish protein structure. The same researchers monitored structure and oxidation level of lipids extracted from both mackerel and horse mackerel. The results showed an increase in the lipid oxidation level during frozen storage in both species, although a decrease after 8 weeks was observed. Indeed, an increase in the intensity of bands located at about 3011 cm^{-1} and 2960– 2850 cm^{-1} of fish oil extracted from the 2 species was observed and attributed by the authors to lipid alterations, involving C-H groups and hydrophobic interactions. Changes in lipid structure were found to be more obvious in freeze-dried mackerel oil compared to freeze-dried horse mackerel. The authors attributed this trend to

the formation of primary oxidation products which were found to be significantly higher in mackerel than in horse mackerel.

In another study, Afseth et al. (2006) assessed the potential of Raman spectroscopy to predict unsaturated fatty acid levels, expressed as iodine value. Different batches of salmon samples with naturally varying fatty acid compositions and overall sample heterogeneity (extracted oils, ground salmon samples, and intact samples) were examined in the 790 -1790 cm^{-1} and 2776-3052 cm^{-1} spectral regions. By applying PLSR, the best results were obtained on the extracted oil, since R^2 and RMSECV values of 0.87 and 2.5 g I_2/100 g fat were obtained, respectively. The ground samples provided comparable results giving R^2 and RMSECV of 0.85 and 2.7 g I_2/100 g fat, respectively. Less successful results were obtained on intact salmon muscle, since only average values of 0.74 and 3.33 were obtained for R^2 and RMSECV, respectively. The authors attributed this difference to sampling procedure. These results were recently confirmed by Sanchez-Alonso et al. (2012b) who investigated changes in lipids extracted from hake fillets after frozen storage at -10 °C for 3, 14, and 23 weeks. Lipid oxidation changes occurring at about 1658 cm^{-1} were attributed to *ν* C=C stretching band, which, in turn, was attributed to development of conjugated dienes.

Raman spectroscopy proved to be of potential utility for process line measurements of fish quality. Some advantages of this technique are: (i) nondestructive analytical and structural probe allowing in situ analysis of agricultural and food products; (ii) water shows a weak Raman spectrum that permits to obtain spectra from aqueous solutions or high water content samples; (iii) only a small amount of sample is required; and (iv) spectra can be acquired on solid, fibrous, and liquid samples (Garrigues and Guardia, 2013). There are, however, some drawbacks to this

method: i) measurements require expensive lasers, detectors, and filters; ii) large degree of optical sampling variance when performing the measurement; and iii) various factors such as color, absorbance, scattering, turbidity, and particle size can affect the measurement of a solid sample (Marquardt and Wold, 2004).

Instrumental Sensors as Emerging Methods for Fish Quality Assessment

Up to date, sensory analysis has been considered as the most reliable system to provide information about color, taste, and smell of fish and other seafoods. However, increasing demands on quality monitoring requires an increasing support of sensory methods by instrumental sensors, including electronic nose (e-nose), electronic tongue (e-tongue), and electronic eye (e-eye).

Electronic Nose

The use of human nose as a smell assessment instrument has been still limited due to the fact that our sense of smell is subjective, gets tired easily, and is therefore difficult to use. Consequently, e-nose was developed in order to mimic the function of human nose and bypass these limitations.

A variety of e-noses (e.g., electrochemical gas, metal oxide, conducting polymer sensors, etc.), coupled with different features extraction and data processing methods, have been employed for freshness assessment and other quality parameters of fish and other seafoods. For example, 2 e-noses, namely FreshSense and LibraNose, consisting of, respectively, five electrochemical sensors and eight thickness shear mode resonators, were tested on cod fish fillets stored at 0 °C

over a period of 17 days (Di Natale et al., 2001). In a first step, the authors analyzed separately the data collected from each electronic nose. By applying PLS-DA with leave-one-out cross-validation, misclassifications of storage times were of 33% and 9% for respectively FreshSense and LibraNose sensors. In a second step, data obtained from the two instrumental sensors were analyzed jointly, and the classification rate was improved since misclassification rate of only 4% was observed.

In another study, Haugen et al. (2006) attempted to monitor smoked salmon process at industrial environment using a prototype solid-state-based gas-sensor array system, called FishNose. The FishNose system was equipped with a set of six sensors fulfilling 3 requirements: i) diverse sensor materials; ii) high sensitivity to spoilage compounds; and iii) rapidity of measurement. By using PLSR model, a good correlation between data obtained with gas sensors and those of sensory and microbiological methods was obtained (e.g., R value of 0.81 was observed between LY2/G sensor and smoked salmon odor). Additionally, the FishNose system allowed to classify samples with correct classification rates ranging from 93% to 95% for fresh and aged samples, respectively. However, the authors did not disclose if classification rates were acceptable for quality control purpose.

Other type of e-nose based on 4 integrated metal oxide micro-sensors was developed for sardine freshness evaluation (El Barbri et al., 2009). The authors succeeded in classifying sardine samples into three groups: fresh, medium, and outdated sardines stored for maximum of 2 days, 3 days, and 4 days or more, respectively. Then, the authors applied PLSR to assess the potentiality of e-nose to predict microbiological, and high correlation (R= 0.91) was obtained with total viable counts microorganisms. Additionally, identification of freshness stage was

achieved with 100% accuracy using SVM approach, suggesting the use of e-nose as a simple, reliable, fast, and reproducible technique for fish freshness evaluation.

Recently, Tian et al. (2012) used metal oxide sensors to monitor freshness of hairtail fish kept at different storage temperatures (5, 10, and 15 °C) and storage times (3, 4, and 5 days). High correlations between e-nose and aerobic bacterial counts and TVB-N were observed (R ranged from 0.91 to 0.97). In a similar approach, the shelf-life of European sea bass was predicted using a commercial portable e-nose composed of 10 metal oxide semiconductors (Limbo et al., 2009). By applying PCA and HCA to the data sets, 3 groups were formed, namely, fresh, old, and very old groups. One of the main conclusions of this study was that a decrease of storage temperature by 2 °C, increased the longevity of fish for up to 5–6 days.

Electronic Tongue

E-tongue has emerged as a tool for rapid assessment of complex liquids. It is a device made of sensors responding to some taste (soluble) of foods through the transduction of a signal or a pattern of signals thanks to a pattern-recognition software system. In the literature, different electrochemical sensors including amperometric, potentiometric, and voltammetric sensor arrays have been proposed for this purpose (Cosio et al., 2012).

The range of applications of e-tongue depends largely on the characteristics of the sensors. The main application of this technique in fish and seafood products is related to freshness assessment. For example, e-tongue, comprising 16 potentiometric electrodes of themetal, metal oxide, and insoluble metal salt type was developed to evaluate fish freshness of sea bream stored at 4 °C for up to 14 day (Gil et al., 2008). By applying a special type of ANN approach, 100% correct

classification was obtained. Moreover, PLSR applied to e-tongue data allowed excellent predictions (R > 0.9) of biogenic amines, pH, microbial analysis, and TVB-N. In a similar study, Barat et al., (2008), applied an e-tongue composed of gold and silver wires to monitor sea bream fish stored at 4 °C for up to 15 days. The potentiometric measurements were compared with the results of some references methods (physicochemical, microbiological, and biochemical analyses), and high correlation between the two data sets was obtained, particularly between K-value and e-tongue data (R^2= 0.96).

In order to determine the degree of freshness of tench fillets by monitoring biogenic amines generated during fish degradation processes, Rodríguez-Méndez et al. (2009) compared conventional voltammetric e-tongues based on carbon paste electrodes, with array of screen-printed electrodes. It was evidenced that both systems were sensible to monitor fish spoilage, giving an increased signal related to the formation of biogenic amines during storage time. By applying PCA, PLS-DA, and PLSR approaches, the authors reported that it was possible to classify the day of fish degradation and to predict pH parameter with an excellent accuracy.

Recently, a voltammetric e-tongue was used to evaluate the shelf-life of fresh cod samples (Ruiz-Rico et al., 2013). Results obtained from this study showed that e-tongue data were able to discriminate between fresh (days 0 and 1) and spoiled (from days 4 or more) fish samples. Then the authors applied PLS models to predict some physicochemical and microbial parameters, and rather good results were obtained, especially for TVB-N and mesophilic bacteria, since R^2 values of 0.79 and 0.78 were obtained, respectively. It was concluded that e- tongue technique represented an important advance for assessing the shelf-life of cod fish, rapidly and nondestructively. Recently, the efficiency of e-nose and e-tongue has been confirmed by Han et

al. (2014) on 150 large yellow croaker samples stored at 4 °C for up to 10 days. Three-layer radial basis function neural network, applied separately to each sensor, gave correct classification for the calibration and validation data sets of 87.9% and 80% for the e-nose and 86.3% and 83.8% for the e-tongue, respectively. Then, the authors analyzed jointly the data obtained from the two instruments, and better discrimination was achieved since 94% and 93.9% of correct classification were obtained for the calibration and validation data sets, respectively. The authors suggested that e-nose and e-tongue provided a common description of fish samples throughout storage, allowing their potential use as tools to detect fish freshness nondestructively.

5.3. Electronic Eye

Color is one of the most important quality attributes of fish and other seafood products due to its relation with products freshness, and therefore, has a direct effect on consumer's perceptions. Traditional instruments, such as colorimeters and spectrophotometers, have been used extensively in the food industry for color measurement. However, over the past few years, many instrumental sensors have been integrated in emerging techniques such as computer vision system (CVS) and machine vision system (MVS) for objective color evaluation of fish and other seafood products.

The application of MVS for eyes and gills of stored fish could be a good choice for on-line and noninvasive evaluation of fish freshness. For example, in a recent study (Dowlati et al., 2013), color parameters including lightness (L^*), redness (a^*), yellowness (b^*), total color change (ΔE), and chroma (c^*) were investigated on farmed and wild gilthead sea bream stored in ice for up to 17 days. The obtained results showed that (L^*), (b^*), and (ΔE) of eyes and gills increased with

storage time, while (c^*) decreased in the two species. By applying multiple regression models and ANN approaches, a high correlation was found between color parameters of the two fish species and storage days (R > 0.95). Although color measurements were found to be more precise for gills than those for eyes, the authors recommended the color determination of fish eyes, due to the time needed for removing the gills cover.

In another study, Quevedo et al. (2010) developed a CVS based on *L*a*b** values to assess the color of salmon fillet. A high correlation (R=0.95) between CVS and sensory panel methods was observed, allowing the authors to propose this instrumental color sensor to be used for fishery chain traceability, species identification, and authenticity testing.

The e-eye could also be employed to determine the quality of product by using shape and size parameters. With this regard, a MVS capable of sorting oysters by size and detecting irregular shapes was developed to grade oysters into good quality, banana, and irregular grades based on 50 representative oyster images for each shape category, by using a shape similarity measure called turn angle cross-correlation (Xiong et al., 2010). The results obtained in this study showed a very high shape grading accuracy (96.9%, 100%, and 94.3% for good, banana, and irregular categories, respectively) compared to human grading results.

From the above mentioned results, it could be concluded that instrumental sensors could be considered as excellent alternatives to time-consuming, laborious, and expensive sensorial panels for smell, taste, and appearance evaluation. Moreover, these techniques may be promising methods for detecting quality changes of fish and seafood products nondestructively. However, there remain some fundamental problems to be addressed. One of the greatest technological challenges is still the natural biological variation of raw material of fish and seafood products,

manifested in shape, size, color, texture, and other properties, which occur in some other industrial food applications but to a lesser extent.

Conclusions and Future Trends

During the past decade, considerable interest has been paid to seafood quality and safety and methods of production due to the recent crises and scandals in the food industry which have seriously undermined consumer confidence. Therefore, the need for rapid analytical techniques to measure fish quality, in general, and fish freshness and authenticity, in particular, is greater than ever. Sensory, physicochemical, rheological, and other traditional methods have been used for assessment of quality of fish and other seafoods. However, many of these methods are either time-consuming, destructive, or require trained personnel, and are therefore not suited for online or large-scale operations.

Recently, considerable effort has been made by researchers to explore the possibilities of using spectroscopic techniques for the determination of quality of fish and other seafoods. These techniques (NIR, MIR, FFFS, NMR, and Raman spectroscopies), as well as some instrumental sensors have demonstrated considerable potential to evaluate fish freshness, authenticity, and other quality and safety parameters. They are relatively low-cost and can be applied in both fundamental research and in the factory as on-line sensors for fish process monitoring and product quality assessment. Moreover, these techniques are nondestructive, rich in information on both molecular structures and physical states, and, therefore, provide a fingerprint of the product. The results compiled in this review suggest that the methodology of coupling different

spectroscopic techniques to appropriate chemometric tools could allow characterizing in depth a maximum of information contained in spectral data.

Our literature review revealed that there is no single robust method available which reliably and satisfactorily measures the overall quality of fish and other seafoods. Consequently, none of these techniques has become a routine method in daily practice due to the fact that each method has its particular advantages and disadvantages. Therefore, the use of a range of traditional and more innovative methods, including spectroscopic and other emerging techniques in combination with chemometric approaches could be powerful tools for understanding the molecular and macroscopic bases of food structure and, as a consequence, food quality.

It could be concluded that analyzing jointly data sets collected on samples by using different analytical techniques and chemometric tools offers new possibilities of exploration data without any prior knowledge. Therefore, more attention should be paid to the use of the concept of combined techniques which allows to: i) overcome the deficiencies and limitations of each method; ii) increase the information extracted from the sample; and iii) understand the relationship between the texture determined at the macroscopic level and the structure determined at the molecular level and their impact on fish freshness.

With continued technical innovations in chemometrics software and computer science, the few limitations of spectroscopic techniques and instrumental sensors would be overcome. Future efforts need to be focused on maximizing the potential benefits of the existing techniques, while minimizing their potential drawbacks, and concentrate on developing new improved methods, particularly EEM and synchronous spectroscopies.

It is expected that this review will contribute to build a current picture of the techniques and scientific knowledge used for the assessment of the quality of fish and other seafoods, thus helping to move forward and to support future developments in the seafood industry.

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Table 1: Some examples of traditional methods used for quality assessment of fish and other seafoods

Fish species	Methods/parameters	Research objective	Main results	Reference
Ray fish	TVB-N, TMA-N, K value	Freshness assessment	Significant increase in TMA and TVB-N contents and linear increase in K value during storage	(Ocaño-Higuera et al., 2011)
Bighead carp	Biogenic amines	Effect of freezing on contents of the biogenic amines	Significant decrease in some biogenic amines in samples stored under frozen temperature	(Hong et al., 2013)
Atlantic mackerel	Lipid oxidation products	Prediction of shelf-life	Very good prediction of shelf-life (R^2 = 0.99)	(Maestre et al., 2011)
Largemouth bass and black, and white crappies	Fatty acid composition	Authentication issues (wild/cultured fishes)	Possibility of differentiation between juvenile wild and cultured fishes	(Tritt et al., 2005)

			using 18:2n-6 acid	
Sea bream	Texturometer QTS-25 and transmission electron microscopy	Monitoring changes in texture and structure during postmortem storage	Degradation in muscle tissue due to a rapid proteolysis, associated with increasing loss of texture	(Ayala et al., 2010)
Cod	Hand held device and QIM score	Development of a rapid method to measure the firmness of fish	Good correlation between the instrumental and sensory (QIM) methods (R = 0.84)	(Schubring, 2002)
Blackspot seabream	QIM scheme	Shelf-life evaluations	Rejection of fish after 12-13 days of storage due mainly to the presence of unpleasant odors in skin and gills	(Sant'Ana et al., 2011)

Fish species	Methods/parameters	Research objective	Main results	Reference
Mediterranean anchovy	QIM and Torry schemes	Freshness assessment	Rejection of fish samples after only 5 days of storage	(Pons-Sanchez-Cascado et al., 2006)
Red mullet and goldband goatfish	Several physicochemical indicators (biogenic amines, TVB-N, TBA, peroxide, and others)	Determination of shelf-life	Limits of acceptability: 8 days for goldband goatfish and 11 days for red mullet	(Ozyurt et al., 2009)
Gilthead sea bream	Torrymeter and other methods (QIM, TVC, K value, and others)	Freshness assessment	Torrymeter measurements give the best results for assessing freshness quality and remaining storage life of fish	(Lougovois et al., 2003)
Plaice, whiting, and mackerel	Torrymeter and other methods (physiological and enzymatic)	Authentication issues (fresh/frozen-thawed fish)	Torrymeter gives the best results for the whole fish, while the enzymatic methods	(Duflos et al., 2002)

			are the best for the fillets	

QIM; Quality Index Method, TBARS; Thiobarbituric Acid Reactive Substances', TMA; trimethylamine, TVB-N; Total Volatile Basic Nitrogen, TVC; Total Viable Count.

Table 2: Some examples of spectroscopic techniques used for quality assessment of fish and other seafoods

Fish and other seafoods	Methods	Chemometric tools	Research objective	Main results	Reference
Salmon paté	FFFS	PCA and PLSR	Detection of early stages of lipid oxidation	Clear difference between samples according to both storage times and lipid oxidation levels	(Olsen et al., 2006)
Shrimp	EEM	PARAFAC/SIMCA	Authentication issues (species/origin)	Very good classification rates of samples according to their origin and species	(Eaton et al., 2012)
Color carp	SFS	-	Determination of pyrene in fish gills	High correlation between pyrene concentrations	(Liu et al., 2012)

				and fluorescence intensity	
Cod, mackerel, salmon, and whiting	FFFS	PCA	Monitoring of fish freshness	AAA+NA, tryptophan, and NADH fluorescence spectra are fingerprints of fish freshness	(Dufour et al., 2003)
Whiting	FFFS	PCA and FDA	Authentication issues (storage conditions; light/dark, total/partial vacuum)	Concatenating physicochemical and fluorescence data allows more than 90% of correct classification	(Hassoun and Karoui, 2015)
Whiting	FFFS	PCA and FDA	Authentication issues (fresh/frozen-thawed fish)	NADH fluorescence spectra allow the discrimination between frozen/thawed	(Karoui et al., 2006)

				and fresh fish	
Cod and salmon	VIS/NIR	PCA and PLS	Monitoring of fish freshness	VIS is adapted for cod freshness while NIR is useful for salmon	(Nilsen et al., 2002)
European seabass	NIR	PLS-DA	Authentication issues (wild/farmed fish)	NIR spectra allow the discrimination between wild and farmed fish	(Ottavian et al., 2012)
Atlantic salmon	NIR	PCA and PLS	Prediction of microbial spoilage	Good prediction of bacterial number	(Tito et al., 2012)
Halibut	HSI	PCA and SVM	Authentication issues (fresh/frozen-thawed fish)	HSI achieves a correct classification rate of 97.22 % when combined with textural variables	(Zhu et al., 2012)
Tuna	NIR	PCA and PLS	Prediction of some chemical	Good correlation between results	(Khodabux et al., 2007)

			parameters	of traditional chemical methods and NIR results	
Pacific oysters	NIR	Linear mixed models	Freshness assessment	Storage time as well as sample odor (rather than its color) are good indicators of freshness	(Madigan et al., 2013)
Whiting	MIR	PCA and FDA	Authentication issues (fresh/frozen-thawed fish)	Application of chemometric tools to three spectral data sets achieves 87.5% of correct classification	(Karoui et al., 2007)
Fish and other seafoods	**Methods**	**Chemometric tools**	**Research objective**	**Main results**	**Reference**
Atlantic bluefin	MIR	PCA and PLS	Predication of some chemical	Good estimation of chemical	(Hernández-Martínez et

tuna, crevalle jack, and Atlantic Spanish mackerel			quality parameters	composition, pH, TVB-N, and oxidation indices	al., 2014)
European sea bass	^{1}H NMR	ANOVA	Authentication issues (wild/farmed fish)	^{1}H NMR allows successful discrimination between wild and farmed fish, based on lipid fraction	(Vidal et al., 2012)
Haddock, saithe, pollack, and cod	^{13}C-NMR	PCA, LDA, and BBN	Authentication issues (fishes species)	Correct classification of 78% of samples belonging to the different species	(Standal et al., 2010)
Horse mackerel, European anchovy,	Raman	PCA	Authentication issues (fresh/frozen-	Good discrimination of fish according to both species and	(Velioglu et al., 2015)

red mullet, bluefish, Atlantic salmon, and flying gurnard			thawed fishes), and species	freshness (number of freezing/thawing cycles)	
Atlantic and horse mackerel	Raman	ANOVA	Changes in lipids and proteins structure during freeze-drying	Alterations in lipid structure, reflected by variations in the intensity of Raman spectroscopy bands	(Sarkardei and Howell, 2007)

AAA+NA; Aromatic-amino-acids+ nucleic-acids, ANOVA; Analysis of variance, BBN; Bayesian belief networks, ^{13}C-NMR; Carbon nuclear magnetic resonance, FFFS; Front-face fluorescence spectroscopy, MIR; Mid-infrared spectroscopy, NADH; Nicotinamide adenine dinucleotide, SFS; Synchronous fluorescence spectrophotometry, EEM; Excitation emission matrix, ^{1}H NMR; Proton nuclear magnetic resonance, LDA; Linear discriminant analysis, NIR;

Near-infrared, PCA; Principal component analysis, SIMCA; Soft independent modeling of class analogy, SVM; Support vector machine, VIS; Visible.

Table 3: Some examples of instrumental sensors used for quality assessment of fish and other seafoods

Fish and other seafoods	Methods/parameters	Research objective	Chemometric tools	Main results	Reference
Cod	E-nose (FreshSense and LibraNose)	Freshness assessment	PLS-DA	Correct classification rate of 96% was obtained when analyzing jointly data from the 2 instrumental sensors	(Di Natale et al., 2001)
Salmon	E-nose (FishNose)	Monitoring smoking process	PLSR	High correlation between e-nose data and sensory and microbiologica	(Haugen et al., 2006)

				l methods	
Sardines	E-nose (metal oxide micro-sensors)	Freshness assessment	SVM	Classification of fish freshness with 100% accuracy High correlations between microbiologica l and e-nose	(El Barbri et al., 2009)
Europea n sea bass	E-nose (metal oxide semiconductors)	Prediction the shelf-life	PCA and HCA	Decreasing storage temperature by 2 °C, induced an increase of the shelf-life of 5–6 days	(Limbo et al., 2009)
Sea bream	E-tongue (potentiometric)	Evaluation of fish freshness	ANN and PLSR	Correct classification	(Gil et al., 2008)

		and prediction of some traditional quality parameters		rate of 100%, and excellent predictions (R > 0.9) of the traditional parameters	
Sea bream	E-tongue (potentiometric)	Freshness assessment	ANOVA	High correlation between e-tongue data and K value, (R^2= 0.96)	(Barat et al., 2008)
Fish and other seafoods	**Methods/parameters**	**Research objective**	**Chemometric tools**	**Main results**	**Reference**
Tench	E-tongue (voltammetric)	Freshness assessment	PCA and PLS-DA	Successful monitoring of fish freshness based on biogenic amines	(Rodríguez-Méndez et al., 2009)

				evolution, and prediction of parameters such as the pH with an excellent accuracy	
Large yellow croaker	E-nose and e-tongue	Freshness assessment	Radial basis function network	More than 90% of correct classification was obtained by analyzing data from the 2 instrumental sensors	(Han et al., 2014)
Gilthead sea bream	E-eye (MVS)	Freshness assessment based on color evolution of eyes and gills of fish	Regression models and ANN	Changes in eye color were found to be significantly correlated with days of storage ($R^2 > 0.9$)	(Dowlati et al., 2013)

Salmon	E-eye (CVS)	Fish quality (color measurements)	*t*-test	High correlation between CVS data and sensory analysis (R=0.95)	(Quevedo et al., 2010)
Oysters	E-eye (MVS)	Fish quality (size and shape measurements)	Turn angle cross-correlation	High shape grading accuracy (> 90%) compared to human grading results	(Xiong et al., 2010)

ANN; Artificial neural network, ANOVA; Analysis of variance, CVS; Computer vision system, E-eye; Electronic eye, E-nose; Electronic nose, E-tongue; Electronic tongue, HCA; Hierarchical cluster analysis, MVS; Machine vision system, PCA; Principal component analysis, PLS-DA; Partial least squares discriminant analysis, PLSR; Partial least squares regression, SIMCA; Soft independent modeling of class analogy, SVM; Support vector machine.

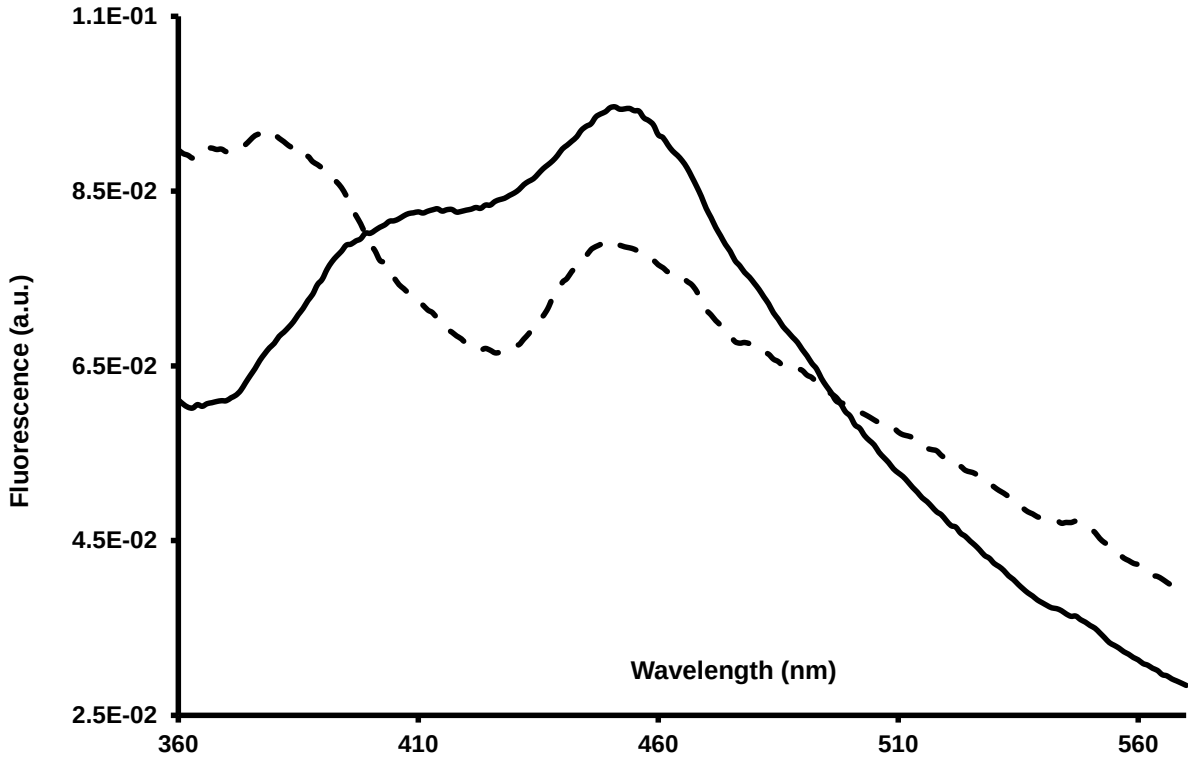

Fig.1. Normalized NADH fluorescence spectra (excitation 340 nm, emission 360–570 nm) of fresh and frozen–thawed fish fillets

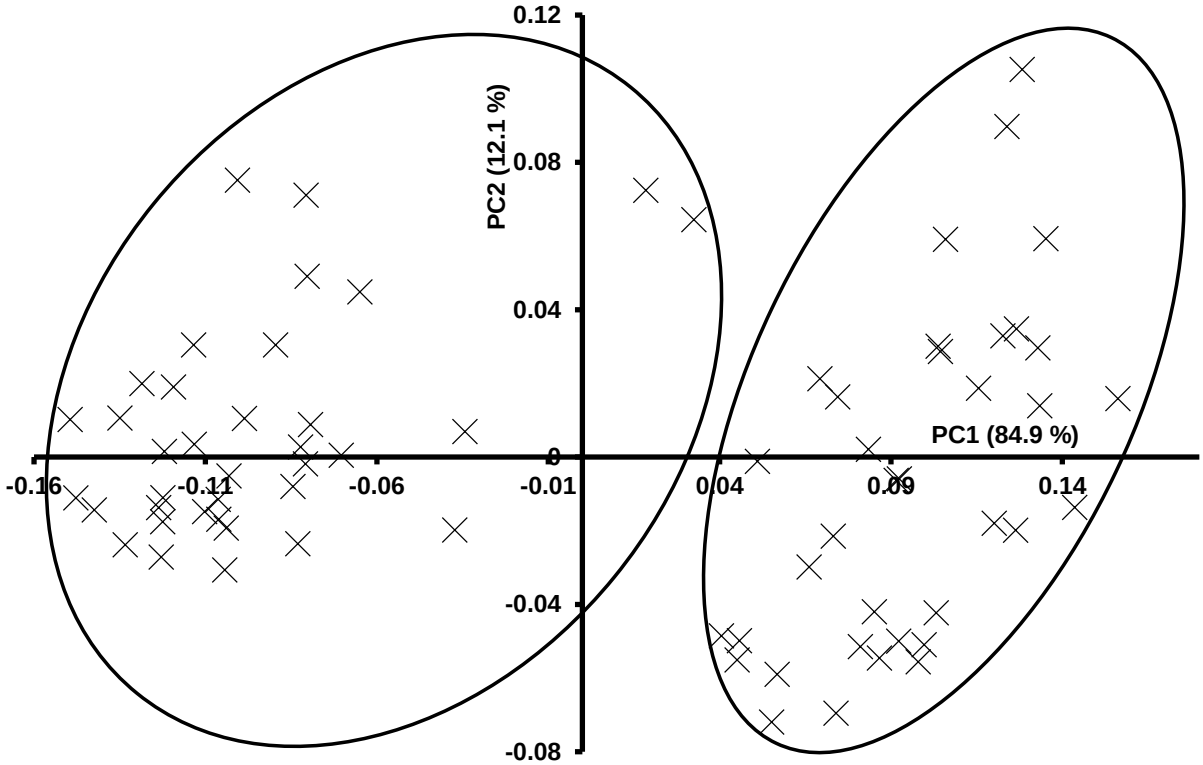

Fig.2. Principal component analysis similarity map determined by principal component 1 (PC1) and principal component 2 (PC2) for the NADH fluorescence spectra of fresh and frozen–thawed fish fillets

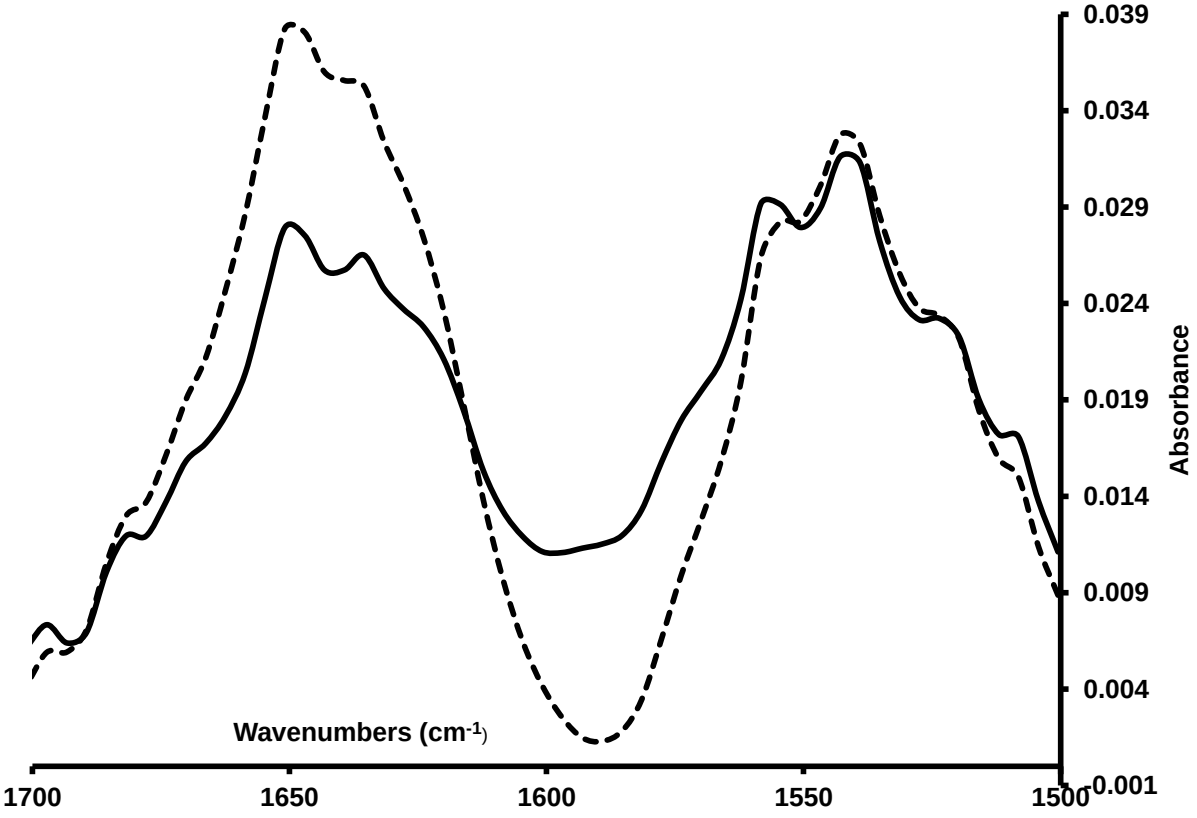

Fig.3. Normalized mid-infrared spectra recorded in the 1700-1500 cm^{-1} spectral region of fresh and frozen-thawed fish fillets.