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Monitoring changes in whiting (*Merlangius merlangus*) fillets stored under modified atmosphere packaging by front face fluorescence spectroscopy and instrumental techniques

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ABSTRACT

Quality assessment of whiting (*Merlangius merlangus)* fillets stored in normal air (control group) and modified atmosphere packaging (MAP1: 50% N_2/50% CO_2 and MAP2: 80% N_2/20% CO_2) for up to 15 days at 4 °C was performed. The physico-chemical [pH, drip loss, moisture content, total volatile basic nitrogen (TVB-N), thiobarbituric acid reactive substances (TBARS) and peroxide value (PV)], textural (i.e., hardness, fragility, gumminess, chewiness, springiness, cohesiveness), and color (i.e., L^*, a^*, b^*) parameters were determined. Front face fluorescence spectroscopy (FFFS) emission spectra were also scanned on the same samples with excitation set at 290 and 360 nm. The results indicated that MAP treatment, particularly MAP1 had an obvious preservative effect on fish quality by reducing pH value, TBARS and TVB-N contents, and retarding the softening of fish texture compared to control samples. Principal component analysis (PCA) applied to physico-chemical and instrumental data sets showed a clear discrimination of fish samples according to both their storage time and condition. A complete (100%) of correct classification was obtained by the concatenation of spectral, physico-chemical, and instrumental data sets. The results demonstrated that storage under MAP can be recommended to improve quality of whiting fillets, which in turn, can be evaluated by FFFS as a rapid and non-destructive technique.

1. Introduction

The beneficial effects of consumption of fish and other seafoods on health have attracted much attention among scientists and nutritionist. However, the shelf-life of fish and fishery products is usually limited by microbiological and/or chemical deterioration. Therefore, in order to preserve freshness and other quality parameters, such products must be subjected to proper preservation techniques after caught. To this end, many traditional methods such as refrigerating and freezing (Aubourg, Sotelo, & Gallardo, 1997; Calanche et al., 2013), smoking and salting (Guizani, Rahman, Al-Ruzeiqi, Al-Sabahi, & Sureshchandran, 2014; Nguyen, Thorarinsdottir, Thorkelsson, Gudmundsdottir, & Arason, 2012) have been used. Recently, some natural preservatives (antimicrobials and/or antioxidants) such as rosemary oil (Gao et al., 2014), grape seed and clove bud (Shi, Cui, Yin, Luo, & Zhou, 2014), grape seed extract and tea polyphenols (Li, Li, Hu, & Li, 2013) have been used to preserve the quality and thus extend the shelf life of several fish species.

Due to consumer demand for fresh, safe, attractive, easy-buy, easy-consume product, with a prolonged shelf life, modified atmosphere packaging (MAP) has grown in recent years as an efficient method to delay microbial growth and enzymatic spoilage. This method is considered suitable for extending the shelf life of various food products such as dairy products and eggs (Karoui, Mouazen, Ramon, Schoonheydt, & Baerdemaeker, 2006; Karoui, Mouazen et al., 2006; Karoui, Schoonheydt, Decuypere, Nicolaï, & De Baerdemaeker, 2008), red meat and poultry (Arvanitoyannis & Stratokos, 2012), fruits and vegetables (Sandhya, 2010). Modification of the composition within the package by increasing the levels of CO_2 and/or N_2 and thus decreasing the O_2 concentration has demonstrated its ability to prolong the shelf life of several fish species: sea bass (Provincial et al., 2010; Turan & Kocatepe, 2013), gutted farmed bass (Torrieri, Cavella, Villani, & Masi, 2006), and turbot (Santos et al., 2013).

There have been many studies investigating the effects of MAP in combination with other preservation treatment such as

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freeze-chilling for whiting, mackerel, and salmon (Fagan, Gormley, & Úı Mhuircheartaigh, 2004), phenolic compounds for tuna slices (Thiansilakul, Benjakul, & Richards, 2013), ozonated water for red mullet (Bono & Badalucco, 2012), salt and oregano essential oil for sea bream (Goulas & Kontominas, 2007a), and vacuum packaging for chub mackerel (Goulas & Kontominas, 2007b).

Fish quality is a complex concept, including a range of factors, which depend on consumers' quality perception, market preferences, storage conditions, microbial load and activity, etc. However, freshness is the most important quality attributes and control methods for the fish sector. Many traditional methods have been used to monitor freshness and other quality changes occurring in fish during their storage (Hassoun & Karoui, 2015a; Zhao, Li, Wang, & Lv, 2012). Sensory analysis has been widely employed by the inspection services to evaluate freshness of fishery products (Calanche et al., 2013). In general, the sensory quality of fish and other seafoods is evaluated through flavor, odor, color, and texture criteria. Although flavor and odor are highly important parameters allowing to determine fish quality, texture and color remain the major sensory characteristics to be also used. Several physico-chemical parameters such as pH, oxidation index, amine and volatile compounds, *K*-value, etc. (Calanche et al., 2013; Goulas & Kontominas, 2007a; Goulas & Kontominas, 2007b; Li et al., 2013; Santos et al., 2013) have been also used as indicators of fish quality. Although the aforementioned techniques are important, they are destructive, time-consuming and need skilled operators. Moreover, they are expensive and could not be applied when many samples need to be analysed on- or at-line in the food industry (Karoui, Dufour, Schoonheydt, & De Baerdemaeker, 2007; Karoui, et al., 2007). Recently, more attention has focused on the development of non-destructive instrumental techniques such as spectroscopic ones, particularly front face fluorescence spectroscopies (FFFS). Indeed, FFFS is characterized by its high specificity and sensitivity and could provide information on the presence of fluorescent molecules such as tyrosine, phenylalanine and tryptophan residues in proteins, vitamin A in fat globules and their environment in biological samples (Karoui, Schoonheydt, Decuypere, Nicolaï, & De Baerdemaeker, 2007; Leriche et al., 2004; Svensson & Andersen, 2014).

Whiting is known to be one of the highly commercial and nutritional fish species due to its high levels of good-quality proteins and the presence of many vitamins and minerals. Although being lean fish and has little amounts of fat, whiting contains high amounts of polyunsaturated fatty acids (such as eicosapentaenoic and docosahexaenoic acids), which are reputed to reduce the risk of cardiovascular disease. However, very few studies have been carried out on the handling, processing, and preservation treatments of this fish species. Cosansu, Mol, Ucok Alakavuk, and Ozturan (2013) pointed out the effect of lemon juice on shelf life of salted pasteurized whiting fish stored under vacuum packaging. Recently, FFFS has been applied to monitor the whiting fish fillets freshness stored under different conditions of light and vacuum packaging (Hassoun & Karoui, 2015b). However, no reports were found in relation to the use of FFFS for the monitoring of whiting fish fillets under MAP. Thus, the aims of this work were to apply different instrumental methods for monitoring whiting fillets quality stored at 4 °C in different MAP to investiagte the: (i) impact of different storage conditions (2 MAP and 1 control) on the evolution of whiting fillets quality; and (ii) potentiality of FFFS as a rapid technique allowing to determine the whiting fillets freshness, regardless of the storage conditions. Principal component analysis (PCA) and factorial discriminant analysis (FDA) were applied to the different data sets allowing to explore the possibility and feasibility of FFFS to determine the freshness of whiting fillets in different storage conditions.

2. Materials and methods

2.1. Fish samples preparation

Whiting fish samples (*Merlangius merlangus*) were taken at Boulogne-sur-Mer harbour (France) just after unloading of trawler. The average length and weight of the samples were 25 cm ± 3 and 90 g ± 12, respectively. Fish samples were headed, eviscerated, washed thoroughly of blood and filleted within two hours after slaughter. Fish fillets were stored in ice and brought to the laboratory, and then stored at 4 °C until the next day. One fillet was analysed on day 1 and considered as fresh and the remaining fillets were split into three groups: One batch was packaged in normal air and considered as control, and the two others were packaged in modified atmospheres. The gas mixtures used were 50% N_2/50% CO_2 for MAP1 and 80% N_2/20% CO_2 for MAP2 (Aligal, Air Liquide, France). After packaging in polyethylene bag (PA/PE 90), all the samples were stored immediately at 4 °C. Three fillets were taken per sampling day, and analyses were performed on days 3, 6, 8, 13, and 15.

2.2. Physico-chemical analysis

2.2.1. Chemical composition

A proximate composition analysis was performed on fish on day 1 of storage. Proximate analyses (moisture, total crude protein, ash, and lipid contents) of the fish samples were determined according to AOAC methods (AOAC, 1997).

2.2.2. Drip loss

Drip loss was measured gravimetrically. Fillet samples were weighed prior to packaging and at each sampling day. The ratio between mass difference and initial mass of the fillet was determined and expressed as the percentage of drip loss.

2.2.3. pH measurements

The pH value was measured directly on whiting fillet using a digital pH meter (WTW pH 330i Taschen-pH-Meter, WTW GmbH). Prior to pH measurements, the pH meter was calibrated with standard pH solutions prepared using buffer capsules.

2.2.4. Lipid oxidation measurements

Lipid oxidation was assessed by PV and TBARS value. These indexes were measured by iodometric titration and colorimetric methods, respectively for the PV and TBARS (Guizani et al., 2014). The PV were expressed as milliequivalents of peroxide oxygen/kg of whiting fillets (meq./kg of whiting fillets), while results of the TBARS were expressed as milligrams of malondialdehyde equivalents/kg of whiting fillet (mg MDA eq./kg of whiting fillets).

2.2.5. TVB-N content

TVB-N content was determined following the official method proposed by the Commission Regulation (EC) No 2074/2005, and the results were expressed as mg TVB-N/100 g of whiting fillet.

2.3. Instrumental techniques

2.3.1. Color measurements

The color of fish fillets was measured with the Minolta Chroma Meter version CR-300 (Konica Minolta Sensing Europe, Roissy Charles De Gaulle, France) according to the method described by Botosoa, Chénè, & Karoui, 2013a, 2013b and Gao et al. (2014). Measurements were performed directly on fish fillets and the lightness (L^*) (0 = dark, 100 = white), yellowness (b^*) (+60 = yellow, −60 = blue), and redness (a^*) (+60 = red, −60 = green) values were