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Front-face fluorescence spectroscopy coupled with chemometric tools for monitoring fish freshness stored under different refrigerated conditions

Abdo Hassoun, Romdhane Karoui*

Universite d'Artois, Institut Régional en Agroalimentaire et Biotechnologie Charles Viollette, Equipe Qualité et Sécurité des Aliments (QSA), Unité Ingénierie de Formulation des Aliments et Altération, Faculte des Sciences Jean-Perrin, Rue Jean Souvraz, 62307 Lens, France

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ABSTRACT

Front-face fluorescence spectroscopy was used as a rapid tool for assessing freshness of whiting fish (*Merlangius merlangus*) fillets stored at 4 ± 1 °C for up to 12 days under different conditions. Some physicochemical analysis [i.e., water content, pH, peroxide value, thiobarbituric acid reactive substances (TBARS)] were performed. With increasing storage time, the TBARS and pH values increased progressively in all whiting fish fillets, in particular for those exposed to light. Principal component analysis and factorial discriminant analysis applied separately to the tryptophan (excitation: 290 nm, emission: 305–450 nm) and nicotinamide adenine dinucleotide (NADH) (excitation: 340 nm, emission: 360–600 nm) spectra gave only a slight discrimination between the investigated whiting fish fillets. These results were improved when data from all the fluorescence spectra were analyzed jointly, since nearly three-quarters of samples were correctly classified. The best results were obtained by concatenating the fluorescence and physicochemical data sets, giving more than 90% of correct classification.

1. Introduction

Fish and fishery products play an important role in human nutrition, and their consumption has been associated with several health benefits. However, fish is a highly perishable product, so adequate preservation techniques must be used to maintain the desired levels of quality and safety throughout storage. Storage of fish at low temperature and/or by using suitable packaging can for example reduce lipid oxidation and thus prolong its shelf-life. Recently, conventional packaging materials such as flexible plastic films and thermoformed containers are commonly used. However, even with the new forms of packaging and distribution, fish and fishery products still undergo chemical deterioration and microbial spoilage.

Oxidation is one of the major causes of quality deterioration in fish muscle that is initiated by several factors such as exposure to light and air, heat, enzymes, metals, metalloproteins, and microorganisms (Shahidi & Zhong, 2005). For example, exposure to light during processing, distribution and retail storage is known to initiate oxidation processes resulting in nutrient loss, discoloration and formation of off-flavors in dairy products (Andersen, Vishart, & Holm, 2005).

Fish quality is a complex concept, including a range of factors, which depend on consumers' quality perception, market preferences, storage conditions, etc. However, fish freshness is considered to be of major importance to all consumers and one of the most relevant qualities attributes. Therefore, much attention has been given to find a rapid and reliable method for fish freshness assessment. A large variety of traditional methods has been proposed in the literature including physicochemical (e.g., oxidation indices, biogenic amine and volatile compounds, and K-value), microbiological, textural, and sensory techniques (Atrea, Papavergou, Amvrosiadis, & Savvaidis, 2009; Casas, Martinez, Guillen, Pin, & Salmeron, 2006; Ocaño-Higuera et al., 2011; Özyurt, Kuley, Özkütük, & Özogul, 2009). Although the above-mentioned methods provide useful information on the evaluation of fish freshness and are extensively used as referential methods, they require sophisticated analytical equipment and skilled operators. Moreover, they are time consuming and, therefore cannot fulfill the demand of rapid screening that industry needs. On the other hand, spectroscopic method, in particularly front-face fluorescence spectroscopy (FFFS) have been used as rapid screening

* Corresponding author. Tel.: +33 3 21 79 17 00; fax: +33 3 21 79 17 17.
E-mail address: romdhane.karoui@univ-artois.fr (R. Karoui).

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techniques to assess fish quality. The main advantages of such techniques are rapid sample data acquisition, the potential to determine several parameters simultaneously, and the capacity to replace expensive and time consuming reference techniques (Karoui & Blecker, 2011; Karoui, Lefur, et al., 2007; Karoui, Mouazen, Ramon, Schoonheydt, & De Baerdemaeker, 2006).

The potential of FFFS technique to evaluate fish freshness has been increased with the propagated application of chemometric tools. For example, Dufour, Frencia, and Kane (2003) have used this technique to monitor fish freshness by examining the fluorescence properties of NADH and aromatic amino and nucleic acids recorded on cod, mackerel, salmon and whiting fillets. In a similar approach, Karoui, Thomas, and Dufour (2006) investigated the potential of tryptophan and NADH fluorescence spectra to differentiate frozen/thawed from fresh whiting fish fillets.

Whiting is considered 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 acid and docosahexaenoic acid), which are reputed to reduce the risk of cardiovascular disease. Some studies have been carried out on the handling, processing and preservation treatments of this fish species. For example, Cosansu, Mol, Ucok Alakavuk, and Ozturan (2013) determined the impact of dipping whiting fish samples in the freshly lemon juice on shelf life of salted pasteurized samples stored under vacuum packaging.

To our best knowledge, there is no information available in the literature on the effect of light and vacuum packaging during storage of whiting fillets. Thus, the objective of this study was to evaluate the potential of FFFS for monitoring whiting fillets freshness during 12 days of storage at 4 °C in the: i) presence of light and darkness; ii) total and partial vacuum packaging. As the use of chemometric tools is usually required for interpretation of the data sets, multidimensional analysis such as principal component analysis (PCA) and factorial discriminant analysis (FDA) were used.

2. Materials and methods

2.1. Chemicals and reagents

All chemical products used in this study were of analytical grade. Xylenol orange tetrasodium salt (powder) and cumene hydroperoxide (CuOOH, 80%) were purchased from Alfa Aesar (Germany). Ammonium iron (II) sulfate hexahydrate, sulfuric acid (95%), sodium sulfate anhydrous, Celite® 545, hexane, isopropanol, and boric acid were obtained from VWR International, while methanol (for analysis), 2-thiobarbituric acid (99%), trichloroacetic (99.5)%, and sodium hydroxide (NaOH, 40%) were procured from MERCK, Darmstadt, Germany.

2.2. Preparation, packaging and storage of fish samples

Twenty one (21) whiting fish samples were taken at Boulogne-sur-Mer harbor just after unloading of trawler. The fishes were filleted, kept in plastic film to protect them from the ice and brought to the laboratory within a 2 h in iced condition. Upon arrival, samples were kept at 4 °C until the next day when one sample was analyzed on day 1 and considered as fresh. Fish samples were packaged in polyethylene bag (PA/PE 90) and stored under different conditions. Four storage conditions were tested: i) five samples kept in the dark and packed in partial vacuum (DPV); ii) five samples kept in the dark and packed in total vacuum (DTV); iii) five samples exposed to light and packed in partial vacuum (LPV); and IV) five samples exposed to light and packed in total vacuum (LTV). The PV (pressure ~ 0.738×10^5 Pa) and TV (pressure ~ 0 Pa) were applied using a vacuum sealer (model MULTIVAC from Guy DEREGNAUCOURT, Orchies, France). All the samples were kept in an open chiller showcase at ~4 °C. Half ($n = 10$) of the samples was exposed to light (light source of 7 W) and the remaining 10 samples were covered with aluminum foil to protect them from the light. One sample of each condition was analyzed on days 3, 5, 8, 10, and 12 of storage.

2.3. Physicochemical analysis

2.3.1. Water content determinations

Water content was determined by weighing before and after complete desiccation during 24 h at 105 °C (Air Concept, FIRLABO, Emerainville, France). Analyses were performed in triplicate.

2.3.2. Protein content measurements

Total nitrogen was estimated by Kjeldahl method; About 2 g of sample was digested with 10 ml of concentrated sulfuric acid with a pinch of digestion mixture (potassium sulfate, copper sulfate, and titanium dioxide) in a 250 ml digestion flask. The sample was then distilled along with strong alkali (NaOH) and the ammonia liberated was absorbed in 30 ml boric acid (40 g/l). The receiving solution containing ammonium borate was titrated with standard H_2SO_4 (0.1 N). A blank was also run side by side and the concentration of nitrogen in the sample was determined as follows:

$$\text{Nitrogen\%} = 1.4007 \times (\text{mL HCl sample} - \text{mL HCl blank}) \times \text{normality HCl/g sample}$$

Crude protein content was determined by multiplying total nitrogen by a factor of 6.25.

2.3.3. Fat content measurements

Total lipids was extracted according to the "Association Française de Normalisation" AFNOR, (1991). Fish samples were ground to a homogenous mixture with a commercial blender (Waring commercial Blender, Connecticut, USA). To extract fat from crushed fish (~45 g), a volume (250 mL) of hexane/isopropanol (3/2) (v/v) was used. In order to increase the extraction yield, the mixture was stirred with a magnetic stir bar for ~30 min at ambient temperature (~20 °C). Then, the fat extract was eluted and separated from the solid residue by passing it through a 2 cm high column of Celite and sodium sulfate laid on the bottom of a Büchner filter. The filtrate was dried in a rotary evaporator (Büchi, Rotavap R-3) at speed 4. Bath temperature was previously equilibrated at 40 °C which corresponds to the fat melting point, while the cooling was set at 5 °C. Fat content was expressed as g/100 g of whiting flesh.

2.3.4. pH measurements

Two grams (2 g) of fish muscles were homogenized in five volumes of distilled water in an Ultra-Turrax (T 25 digital ultra Turrax – IKA) at 4000 rpm for 60 s. The pH value of homogenate filtrate was measured with 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.

2.3.5. Primary and secondary lipid oxidation products

2.3.5.1. Peroxide value measurements. Hydroperoxide content was determined according to a modified xylenol orange method (Eymard & Genot, 2003); 3 g of whiting fish fillets were added to 30 ml of methanol. The mixture was homogenized for 15 s at 20,000 rpm with an Ultra-Turrax (T 25 digital ultra Turrax – IKA). The obtained homogenates were centrifuged for 10 min at