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Predictive modelling and selection of Time Temperature Integrators for monitoring the shelf life of modified atmosphere packed gilthead seabream fillets

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ABSTRACT

The objective of the present study was to validate a kinetic model for growth of spoilage bacteria in modified atmosphere packed (MAP) gilthead seabream fillets and to select a Time Temperature Integrator (TTI). The temperature and CO_2 dependence of the growth of lactic acid bacteria in MAP gilthead seabream fillets was expressed by an Arrhenius-type model for the range of 0–15 °C and 20–80% CO_2, which was validated at isothermal, variable and chill chain conditions. A new UV activatable photochemical TTI, was kinetically studied and the influence of the level of activation on the response of the TTI was modelled. Applying the developed models, the required charging levels were estimated so that the TTI response was tailored to monitor the shelf life of fish fillets at selected MAP conditions, during the chill chain storage. A simulation experiment of the product distribution and storage in various chill chain conditions showed the applicability of the TTIs as shelf life monitors.

1. Introduction

The limited and variable shelf life of chilled fish, mainly due to bacterial activity, is a major problem for their quality assurance and commercial viability. Gilthead seabream is one of the most cultured species in the Mediterranean area and its production in Greece was estimated at 44054 tons in 2006, with Greece being the leading world producer with the 47.9% of the total Mediterranean production for gilthead seabream and seabass (FAO, 2006).

Modified atmosphere packaging (MAP) can effectively alter and delay the spoilage process and extend the shelf life of fresh fish (Torrieri, Cavella, Villani, & Masi, 2006). CO_2 inhibits the development of the respiratory organisms like *Pseudomonas* sp. and *Shewanella putrefaciens* and the microflora is dominated by Gram-positive organisms, mainly lactic acid bacteria (Sivertsvik, Jeksrud, & Rosnes, 2002). Lactic acid bacteria have been used as a good spoilage index of modified atmosphere packed fish such as chub mackerel (Stamatis & Arkoudelos, 2007), swordfish (Pantazi, Papavergou, Pournis Kontominas and Savvaidis, 2008) and eel (Arkoudelos, Stamatis, & Samaras, 2007). Drosinos, Lambropoulou, Mitre, and Nychas (1997) reported a co-dominance of lactic acid bacteria and *Brochothrix thermosphacta* in gilthead seabream stored under MA (40% CO_2).

Despite the increasing importance of MAP technology in fish industry and the several studies evaluating the effect of MAP on fish products (Dalgaard, Mejlholm, & Huss, 1997; Lyhs, Lahtinen, & Schelvis-Smit, 2007; Özogul, Polat, & Özogul, 2004; Pantazi, Papavergou, Pournis, Kontominas, & Savvaidis, 2008; Stamatis & Arkoudelos, 2007; Torrieri et al., 2006), a limited number of models including the combined effect of temperature and gas concentration in the packaging environment, that could be vital for shelf life optimization and improvement of the chill chain management,have been proposed for spoilage microorganisms (Dalgaard, 1995; Koutsoumanis, Taoukis, Drosinos, & Nychas, 2000). An Arrhenius-type model was developed by Tsironi, Tsevdou, Velliou and Taoukis (2008) as an effective tool for predicting gilthead seabream (*Sparus aurata*) fillet quality and shelf life under different chilled storage temperatures (0–15 °C) and modified atmospheres (20–80% CO_2).

Effective control of the chilled distribution of fresh fish products is vital to their commercial viability. A substantial portion of chilled products are exposed, throughout the distribution, to effective temperatures that deviate significantly from the recommended range. Application of an optimized quality and safety assurance system for the chilled distribution of products would require continuous monitoring and control of storage conditions, from production to consumption (Tsironi, Gogou, Velliou, & Taoukis, 2008).

Time Temperature Integrators (TTIs) can show an easily measurable, time and temperature dependent change that

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cumulatively reflects the time–temperature history of the food product (Taoukis & Labuza, 2003). In order to use a TTI based system effectively, mathematical models are needed that describe the effect of temperature on the evolution of spoilage under dynamic storage conditions. Additionally, a full kinetic study of the TTI response is needed. Based on reliable models of the shelf life and the kinetics both of the product and the TTI response, the effect of temperature can be monitored, and quantitatively translated to food quality, from production to the point of consumption (Taoukis & Labuza, 1989a,b; Taoukis, 2001). A TTI based system could lead to realistic control of the chill chain, optimization of stock rotation and reduction of waste and efficient shelf life management.

The objective of this study was to validate the model that predicts the LAB growth and consequently the shelf life of modified atmosphere packed gilthead seabream fillets (*S. aurata*) as a function of packaging and refrigerated storage conditions. The response of UV activatable TTIs was kinetically modelled as a function of activation level and temperature in order to define the appropriate TTIs that can monitor the quality of fish fillets under any selected storage conditions in the range studied. The applicability of the selected TTIs in the real chill chain was also validated by a simulation experiment of the product distribution and storage in various chill chain conditions.

2. Materials and methods

2.1. Kinetic study of LAB growth on MAP gilthead seabream fillets and validation of the predictive model under isothermal and dynamic conditions

Marine cultured gilthead seabream (*S. aurata*) fillets (weight: 90 ± 10 g, culture zone: Aegean Sea, Greece) came from the same batch and were provided by a leading Greek aquaculture company. Fish was cultivated in net cages and harvested (age 16–20 months). After being ice shocked, fish was put into ice (0 °C), size sorted and transported to the filleting line within 10 h after catch. Fish was scaled, headed, filleted and rinsed with tap water in the industrial filleting line of the company. Fillets were transported directly to the laboratory in polystyrene boxes with appropriate quantity of flaked ice (0 °C, ice/fish ratio 0.5:1 w/w) within 2–4 h. A polyethylene film was placed between fillets, to avoid contact between skin and meat sides of the fillets. Proximate analysis was performed on 5 fillets upon receipt (Grigorakis, 2007).

Fish fillets were packed in HDPE pouches in modified atmosphere (35% CO_2-65% air) (Boss NT42N, Bad Homburg, Germany). Two fillets were packed in each package. Gas headspace was analyzed with the CheckMate 9900 O_2/CO_2 device (PBI Dansensor, Ringsted, Denmark). The gas to product volume ratio was 3:1.

All packages were stored at controlled isothermal conditions of 0, 2.5, 5, 10 and 15 °C in high-precision (±0.2 °C) low-temperature incubators (Sanyo MIR 153, Sanyo Electric, Ora-Gun, Gunma, Japan). Temperature in the incubators was constantly monitored with electronic, programmable miniature dataloggers (COX TRACER ®, Belmont, NC). Samples were taken in appropriate time intervals to allow for efficient kinetic analysis of microbial spoilage. Two independent experiments were also carried out at dynamic conditions. A time–temperature scenario was used, that consisted of three, isothermal steps: 8h at 5 °C, 8h at 9 °C and 8h at 12 °C ($T_{eff} = 9$ °C). A type T thermocouple was inserted into the fish flesh and temperature was constantly monitored during storage, in order to confirm the desired set temperature. Total viable count, *Pseudomonas* sp., lactobacilli and *B. thermosphacta* were enumerated by appropriate plate count methods described in Koutsoumanis, Giannakourou, Taoukis, and Nychas (2002). The sensory attributes of raw and cooked fish were evaluated as described by Tsironi and Taoukis (2010), by a trained sensory panel of 8, selected according to ISO 8586-1 (1993) standard and trained using discriminative tests with practice evaluation methods of determining spoilage characteristics in fish fillets (Botta, 1995).

The microbial growth was modelled using the Baranyi Growth Model (Baranyi & Roberts, 1995). For curve fitting the in-house program DMfit of IFR (Institute of Food Research, Reading, UK) was used, kindly provided by Dr J. Baranyi. Kinetic parameters such as the rate (k_{LAB}) of the microbial growth were estimated. The experimentally measured specific growth rates for LAB and the shelf life of gilthead seabream fillets were compared to the values predicted by the Arrhenius-type model previously developed by Tsironi et al. (2008) based on isothermal experiments at several CO_2 levels, other than the one used in the current experiment (Eq. (1)).

$$k_{LAB} = \left(k_{refLAB}\frac{CO_{2max} - CO_2}{CO_{2max}}\right)\exp\left[\frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \quad (1)$$

where CO_2 is the percentage of carbon dioxide, k_{refLAB}, is the specific growth rate at T_{ref} (4 °C, in the absence of carbon dioxide), $CO_{2,max}$ is the nominal maximum CO_2 concentration for LAB growth, T is the temperature in K, E_a is the activation energy of the studied action and R is the universal gas constant. The values of Eq. (1) parameters were determined as $k_{refLAB} = 0.015 \pm 0.003$ h^{-1}, $E_a = 101 \pm 26$ kJ/mol and $CO_{2,max} = 98.3 \pm 23.5\%$.

Based on the limit for LAB growth correlated to the end of the sensory shelf life (Tsironi & Taoukis, 2010; Tsironi et al., 2008) and the dependence of LAB growth on temperature and CO_2 concentration, expressed by the validated combined Arrhenius-type model, an equation for shelf life determination at any temperature and CO_2 level in the package atmosphere was developed (Eq. (2))

$$t_{SL} = \frac{\log N_l - \log N_o}{\left(k_{refLAB}\frac{CO_{2max}-CO_2}{CO_{2max}}\right)\exp\left[\frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]} \quad (2)$$

where t_{SL} is the shelf life (h) of gilthead seabream fillets, $\log N_l = 6$ is the limit LAB load and $\log N_o$ is the initial LAB load.

2.2. Time Temperature Integrators modelling and application

The OnVu™ TTI (Ciba Specialty Chemicals & Freshpoint, SW), a newly introduced solid state reaction TTI, based on the inherent reproducibility of reactions in crystal phase, was used (Patent EP 1049930 B1). Photosensitive compounds such as benzylpyridines are excited and colored by exposure to low wavelength light. This colored state (dark blue) reverses to the initial colorless at a temperature depended rate. The visual end point can be set by comparison to a light blue printed reference (Fig. 1). By controlling the type of the photochromic compound and the length of UV light exposure during activation the length and the temperature sensitivity of the TTI can be set. The OnVu B1 071031 TTI (Ciba Specialty

Fig. 1. Response scale of solid state photochromic OnVu™ TTI.