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Evaluation of Time Temperature Integrators for shelf-life monitoring of frozen seafood under real cold chain conditions



Theofania Tsironi, Marianna Giannoglou, Eleni Platakou, Petros Taoukis*

National Technical University of Athens, School of Chemical Engineering, Laboratory of Food Chemistry and Technology, 5, Iroon Polytechniou, Zografou, 15780, Athens, Greece

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1. Introduction

Intelligent packaging has been defined as "packaging systems which monitor the condition of packaged foods to give information about the quality of the packaged food during transport and storage" (Ahvenainen, 2003). Smart packaging devices, which may be an integral component or inherent property of a foodstuff's packaging, can be used to monitor the quality changes of food from production to the end point (Kerry, O'Grady, & Hogan, 2006). It has been reported that the temperature conditions of the real cold chain deviate significantly from the recommended range, resulting in significant quality loss at different stages, including retail and domestic storage (Giannakourou & Taoukis, 2003; Gogou, Katsaros, Derens, Alvarez, & Taoukis, 2015; Tsironi, Dermesonlouoglou, Giannakourou, & Taoukis, 2009). The variation in temperature conditions during product distribution and storage can significantly increase the rate of quality degradation of food. A cost efficient way to monitor and continuously communicate the temperature conditions of individual food products throughout distribution would be required, in order to indirectly indicate actual state in terms of quality. Time Temperature Integrators (TTI) could be effective tools to fulfill this requirement (Taoukis, 2010). TTI are inexpensive, active "smart labels" that can show an easily

E-mail address: taoukis@chemeng.ntua.gr (P. Taoukis).

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ABSTRACT

The objective of this study was to evaluate and validate a Time Temperature Integrator (TTI) based cold chain management system to monitor the shelf-life of frozen seafood in the real cold chain, from production to the time of consumption. A pilot study was conducted with frozen blueshark slices and arrow squid with attached UV activatable and enzymatic TTI, tailored to monitor the shelf-life of the selected products in the cold chain. The quality level and remaining shelf-life at predetermined times were estimated based on the response of the TTI and the values were compared to actual measured values of selected quality indices. Results confirm the applicability of TTI as effective indicators of frozen seafood quality during their commercial life.

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measurable, time-temperature dependent change that reflects the temperature history of a food product to which it is attached (Taoukis & Labuza, 2003).

Despite the potential of TTI to substantially contribute to improving food distribution, reducing food waste, and benefiting the consumer with more meaningful shelf-life labeling, their applications up to now have not lived up to initial expectations. More research is needed in the area to advance and develop TTI technologies that could help inform stakeholders when food products no longer meet quality or safety-related criteria (Newsome et al., 2014). The most often underestimated requirement when developing and applying a TTI has been the need for acquiring systematic knowledge of the loss of quality during shelf-life of the food system to be monitored, and a method for expressing quantitatively as accurately as possible the important quality-determining phenomena with appropriate kinetic models.

SLDS (Shelf Life Decision System) and SMAS (Safety Monitoring and Assurance System) are TTI based integrated cold chain management systems, alternative to FIFO (First In First Out), that lead to an improved handling of products, in terms of quality and safety risk. These models are based on kinetic growth models of relevant food microorganisms, data of innate product characteristics and time-temperature history of chilled food products (Koutsoumanis, Giannakourou, Taoukis, & Nychas, 2002; Koutsoumanis, Taoukis, & Nychas, 2005; Tsironi, Gogou, Velliou, & Taoukis, 2008). Yoon, Lee, Kim, Kim, and Park (1994) indicated a positive correlation between oxidative stability and TTI colour change using a phospholipid/phospholipase-based TTI in frozen pork.

 $^{^{\}ast}$ Corresponding author at: 5, Iroon Polytechniou, Zografou, 15780, Athens, Greece.

Giannakourou and Taoukis (2002, 2003) evaluated the applicability of selected enzymatic TTI for predicting remaining shelf-life of frozen vegetables at different temperature exposures from production to consumption. The IQ-Freshlabel (www.iq-freshlabel.eu) European project aimed to develop enzymatic and photochromic TTI smart labels for frozen food products. Methodology was developed for selection of the optimum TTI design of specific frozen seafood products and their application was validated in cold chain simulating trials and in pilot studies. The response function of a photochromic and an enzymatic TTI was determined and appropriate labels for monitoring the quality of blueshark and arrow squid during frozen storage were indicated, using validated kinetic models of quality deterioration of the target seafood products (Giannoglou, Touli, Platakou, Tsironi, & Taoukis, 2014). Based on the principles presented by Tsironi, Giannoglou, Platakou, and Taoukis (2015), appropriate TTI targeting any specific frozen food product can be selected using the proposed methodology for shelf-life testing and kinetic modelling of the TTI response.

The objective of this study was to evaluate and validate a TTI based cold chain management system to monitor the shelf-life of frozen seafood. A pilot field study, from production to the point of consumption, was conducted with frozen blueshark (*Prionace glauca*) slices and arrow squid (*Nototodarus sloanii*) with attached UV activatable and enzymatic TTI, tailored to monitor the shelf-life of the selected products in the cold chain, in order to confirm the applicability of TTI as effective indicators of frozen seafood quality during their commercial life.

2. Materials and methods

2.1. Frozen seafood

Frozen blueshark (*Prionace glauca*) slices (origin: FAO 34) and arrow squid (*Nototodarus sloanii*) (origin: FAO 81) were obtained directly by the seafood processing company (KONTOVEROS S.A., Greece). Samples were packed in cardboard packages lined with HDPE film (net weight: 200 g). All samples came from the same batch and were packed for approximately 1 month at -24 °C until packing.

2.2. Time Temperature Integrators (TTI)

Two different TTI types were used, the one was enzymatic and the second a solid state photochromic TTI. The enzymatic indicators are based on a change of colour due to a decrease of pH, result of a controlled enzymatic hydrolysis of a lipid substrate mixed with appropriate pH indicators. The colour change of the Mtype enzymatic TTI (M Check Point[®], VITSAB, Malmo, Sweden) is the result of a controlled enzymatic hydrolysis by a microbial lipase (Rhizopus Oryzae lipase) of a lipid substrate (methylmyristate). To activate the TTI, enzyme and substrate are mixed by mechanically breaking a separating barrier within the device. This initially green coloured TTI progressively turns into yellow/orange, finally reaching a red colour. Different enzyme concentrations (U/L) can be used to provide a variety of response lives. According to Giannoglou, Touli, Platakou, Tsironi, and Taoukis (2014), M-15U and M-10U (i.e. enzyme concentration of 15U/L and 10U/L) were attached on blueshark and squid packages, respectively.

The OnVu[™] TTI (B1 OnVu[™], Bizerba, Germany) is based on the inherent reproducibility of reactions in crystal phase (Patent EP 1049930 B1). Photosensitive compounds, such as spiropyrans, are exposed to low wavelength light leading to their colourization (dark blue). This state returns to an initial colourless state at a temperature dependent rate. By controlling the photochromic compound type and the time of UV light exposure during

activation, TTI shelf-life and temperature sensitivity can be set (Tsironi, Stamatiou, Giannolgou, Velliou, & Taoukis, 2011). The B1 TTI were charged for appropriate times using the Bizerba Desktop Charger (Bizerba GmbH & Co. KG, Balingen, Germany; charging time of 1 s corresponds to energy of 50 mJ/cm²) and subsequently laminated with an optical filter (TTR 70QC) for protection of the TTI from light exposure and thus recharging. Charging was performed at ambient temperature (22 °C) and low humidity conditions (below 40% RH). According to Giannoglou, Touli, Platakou, Tsironi, and Taoukis (2014), B1-0.2 s and B1-0.3 s (i.e. charging time of 0.2 s and 0.3 s) were attached on blueshark and squid packages, respectively.

2.3. Field test design

Thirty five commercial packages were produced for each seafood product. Temperature was continuously monitored by electronic, programmable miniature data loggers (mini NOMAD RFID Temperature Logger, OM-84-TMP,OMEGA Engineering inc., US) placed inside each package. Appropriate TTI were selected and attached on each frozen food sample based on previous shelf-life tests and mathematical models (Giannoglou, Touli, Platakou, Tsironi, & Taoukis, 2014).

All thirty five packages were stored for 56 days in the production warehouse, before transportation and storage in the distribution center (for 73 days). Afterwards, samples were distributed to eight retail outlets in collaboration with a leading supermarket chain. Samples were collected after 84 days of retail storage and transported to the laboratory to simulate the storage conditions of domestic freezers, in high precision low temperature incubators (Sanyo MIR, Sanyo Electric Co, Ora-Gun, Gunma, Japan) at two constant sub frozen temperatures. Samples were stored at -18 °C for 161 days or at -10 °C for 140 days, indicating domestic storage at recommended and abuse temperature conditions, respectively. An indicative time-temperature scenario including the respective sampling times is presented in Fig. 1. The field test design and the overall time of the samples in the cold chain for the samples (i.e. 374 and 353 days) was based on the nominal shelf-life based on the "use by" date (18 months for all products if stored at -18 °C) which does not consider the time-temperature history of the products.

2.4. TTI response measurement

Colour change of all TTI was measured instrumentally using the Eye-one Pro colourimeter (X-Rite, Michigan, USA) at D50 illumination and 2° observation angle conditions. The enzymatic TTI response change can be described by the normalized value (a + b) of the CIELAB scale (Eq. (1))

norm
$$(a + b) = \frac{(a + b) - (a + b)_{min}}{(a + b)_{max} - (a + b)_{min}}$$
 (1)

Eq. (1) represents the M-type TTI response ranging from value of 0 for green to value of 1 for red. The orange-red hue considered as the visual end point of the TTI corresponds to an instrumental value of 0.8. A mathematical model which describes the effect of the enzyme concentration and the storage temperature ($-15 \,^{\circ}$ C to $5 \,^{\circ}$ C) on the response of the enzymatic TTI was developed by Giannoglou, Touli, Platakou, Tsironi, and Taoukis (2014),

$$norm(a+b) = \frac{1}{1 + \exp\left(\frac{k_{1,ref} * C^{-B_1} * \exp\left[\frac{-E_3}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] - t}{k_{2,ref} * C^{-B_2} * \exp\left[\frac{-E_3}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]}\right)}$$
(2)

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