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Research note

Modeling total volatile basic nitrogen production as a dose function in gamma irradiated refrigerated squid rings

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ABSTRACT

The behavior of a chemical spoilage index for marine products (total volatile basic nitrogen – TVBN) was modeled as a function of the irradiation dose in *Illex argentinus* rings stored in refrigeration. The effect of gamma irradiation at 0, 1.8, 3.3 and 5.8 kGy on TVBN was analyzed in vacuum-packed squid rings during storage at 4 ± 1 °C. The modified Gompertz model satisfactorily described TVBN behavior for each irradiation dose ($R^2 > 0.980$; RMSE < 5.7). Gompertz model parameters (μ, A, L) were modeled with dose-dependent second order polynomials, for doses ranging between 0 and 5.8 kGy, in order to develop a complete model that is useful for predicting TVBN as a function of the dose in squid rings. Model validation was carried out using independent data of TVBN in squid rings irradiated at 4.8 kGy. The developed model can be used to predict TVBN production in gamma irradiated squid meat.

1. Introduction

Squid *Illex argentinus* is the most abundant squid species of the South West Atlantic Ocean (Brunetti, Ivanovic, & Sakai, 1999), with average annual catch in Argentina exceeding 166,000 tons (2000–2012 period, MINAGRI, 2013). Squid is highly perishable because of its particular composition, being mainly deteriorated by the action of gram-negative bacteria (Huss, 1999). One of the main chemical changes during storage of marine product used to assess fish and seafood quality is the gradual accumulation of certain volatile amines in the flesh, which include trimethylamine (TMA), dimethylamine (DMA) and ammonia (Huss, 1999). Marine species contain trimethylamine-N-oxide (TMAO), a body fluid freezing-point depressor involved in fish osmotic regulation. TMAO is reduced to TMA by spoilage bacteria and therefore it is used as a spoilage indicator, being responsible of the typical fishy odor developed during spoilage (Huss, 1999; Pedrosa-Menabrito & Regenstein, 1990). DMA is produced from TMAO by intrinsic enzyme activity during frozen and cold storage (Huss, 1999), being produced in equimolar quantities with formaldehyde. It can be considered an effective marker of fish freshness of many white fish species (Connell, 1975; Huss, 1999; Pedrosa-Menabrito & Regenstein, 1990). One of the most widely used parameters to evaluate fish quality is Total Volatile Basic Nitrogen (TVBN), which includes the measurement of TMA, DMA and ammonia (produced by the deamination of amino-acids and nucleotide catabolites) (Huss, 1999). TVBN is considered particularly useful to assess quality of squid (LeBlanc & Gill, 1984; Woyewoda & Ke, 1980). Gamma irradiation is a safe technology for preserving different foodstuffs by means of the inactivation of spoiling and pathogenic bacteria (Josephson, 1983; Urbain, 1986; WHO, 1994, 1999). There have been numerous studies on the shelf-life extension of fish products treated with ionizing radiation (IAEA, 1969; ICGFI, 1991; Kilgen, 2001; Lescano, Kairiyama, Narvaiz, & Kaupert, 1990; Narvaiz, Lescano, Kairiyama, & Kaupert, 1989; Nickerson, Licciardello, & Ronsivalli, 1983), including the inactivation of spoiling bacteria by gamma irradiation in squid (*Illex argentinus*) rings (Tomac et al., 2012, Tomac, Mascheroni, & Yeannes, 2013; Tomac & Yeannes, 2012). The mathematical modeling of TVBN spoilage index behavior with respect to gamma irradiation is important to assess and manage food safety and shelf-life, and is convenient for the food industry since it avoids costs and time related to preliminary irradiation experiences. Modified Gompertz equation (Zwietering, Jongenburger,

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Rombouts, & Van Riet, 1990) is among the most widely used microbial growth primary models (Gibson & Roberts, 1989) and it has also been used to model other biological phenomena, like the growth of blue shrimp (*Penaeus stylirostris*) (Sepúlveda Medina, 1996). The objective of this work was to model the effect of different gamma irradiation doses on the TVBN production in squid rings, during refrigerated storage.

2. Materials and methods

2.1. Raw material source, treatment and storage

Peeled squid (*Illex argentinus*) mantle rings (1.2 ± 0.3 cm wide), pre-treated with a sodium polyphosphate solution (at 1 ± 1 °C) were acquired in Mar del Plata (Argentina). Immediately after capture and before processing, whole squids were maintained at 0–2 °C with ice flakes. Rings samples of 110 ± 2 g (20 rings approx.) were vacuum-packed in heat-sealed bags of LDPE/PA (Cryovac®, 125 μm) with a Minimax 430M machine (Sevivac, Argentina). Samples were transported in polystyrene boxes with cooling gel ice packs to the semi-industrial irradiation facility of the Ezeiza Atomic Centre (National Atomic Energy Commission, Argentina, activity: 2.22×10^{16} Bq). Samples were divided into four lots consisting of 40 samples each, that were gamma irradiated with a Cobalt-60 source at 0, 1.8, 3.3 and 5.8 kGy, respectively (minimum absorbed doses; dose rate: 10.94 kGy/h). Doses were determined with Amber Perspex dosimeters. Irradiated and non-irradiated samples (control, 0 kGy) were stored at 4 ± 1 °C and analyzed before irradiation (day 0) and at 1, 5, 8, 12, 15, 19, 22, 26 and 29 days after irradiation.

2.2. Total volatile basic nitrogen (TVBN) determination

TVBN was determined by the commercial method adapted from the direct distillation method (Giannini, Davidovich, & Lupín, 1979). Results were expressed as mgN 100 g^{-1} of wet sample. Determinations were done in triplicate.

2.3. Modeling TVBN production during refrigerated storage

Experimental data of TVBN curves for each irradiation dose (0, 1.8, 3.3 and 5.8 kGy) were fitted to a primary growth model, the modified Gompertz equation (Zwietering et al., 1990), in which bacterial counts were replaced by TVBN, as indicated in Eq. (1):

$$\text{TVBN} = \text{TVBN}_0 + A \exp\left[-\exp\left(\frac{\mu e}{A}(L-t)\right)+1\right] \quad (1)$$

where TVBN is the value of TVBN at time t and TVBN_0 the value observed the day after irradiation (mgN 100 g^{-1}), μ is the TVBN production rate (mgN 100 g^{-1} day^{-1}), L is the initial phase during which there are no changes in TVBN (days), A is the complete TVBN change over the entire period and e is the Euler number (2.7182). Data was fitted to modified Gompertz equation by non linear regression (using Marquardt algorithm) with OriginPro® version 8.0 software (OriginLab Corporation, Northampton, MA). The fitting and the accuracy of the estimations for experimental data obtained from each radiation dose was evaluated by the Root Mean Square Error (RMSE) and the determination coefficient (R^2). Considering that RMSE is a measure of the discrepancy between the data and the model estimations, a small value would indicate a tight fit of the model. RMSE was calculated using Eq. (2), where X_{ip} is the predicted value, X_i is the experimental value and n is the number of data pairs:

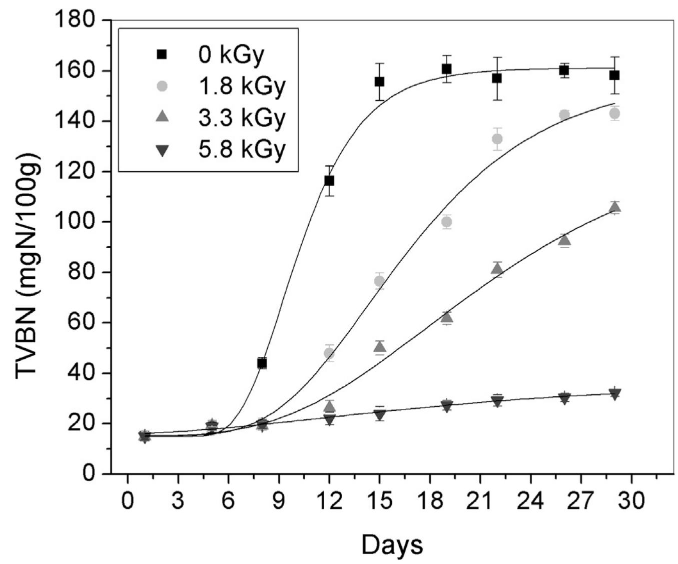

Fig. 1. TVBN (mgN 100 g^{-1}) evolution during storage (4 ± 1 °C) of irradiated and control squid rings (mean ± standard error, $n = 2$). Solid lines represent the modified Gompertz model adjustment.

$$\text{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(X_{ip}-X_i)^2} \quad (2)$$

In order to predict TVBN for different radiation doses it was necessary to find a relationship between Gompertz kinetic parameters (μ, L and A) and the irradiation dose. To develop these secondary models, data were fitted to second order polynomial equations: $\mu = \mu_1 + \mu_2 d + \mu_3 d^2$; $L = L_1 + L_2 d + L_3 d^2$ and $A = A_1 + A_2 d + A_3 d^2$ (where d is the radiation dose). Afterwards, a full model (the complete Gompertz model, **CGM**) was developed by introducing the secondary models into the modified Gompertz equation (Eq. (1)).

The **CGM** fit to experimental data was analyzed by the percentage average relative error (PEr), calculated considering the number of data analyzed (n) by:

$$\text{PEr} = 100\frac{1}{n}\sum_{i=1}^{n}\left|\frac{\text{Experimental value} - \text{Estimated value}}{\text{Experimental value}}\right|$$

2.4. Model validation

The complete model was validated using an independent set of experimental data: TVBN results of squid (*Illex argentinus*) rings treated with gamma irradiation at 4.8 kGy during 77 days of storage at 4 ± 1 °C (Tomac et al., 2012). TVBN values were determined on days 0, 1, 5, 8, 13, 16, 19, 22, 26, 33, 40, 47, 54, 68 and 77. Complete model TVBN predictions were plotted against experimental values in order to analyze the goodness of the predictions.

2.5. Statistical analyses

A two-ways ANOVA test ($p < 0.05$) was used to analyze the significance of irradiation dose (0, 1.8, 3.3 and 5.8 kGy), days of storage (0, 1, 5, 8, 12, 15, 19, 22, 26 and 29 d) and interaction between them. Tukey test was used to compare means ($p < 0.05$). The R-project software (R Development Core Team, 2008) was used.