



Shelf life modelling of frozen shrimp at variable temperature conditions

Theofania Tsironi, Efimia Dermesonlouoglou, Maria Giannakourou, Petros Taoukis*

National Technical University of Athens, School of Chemical Engineering, Laboratory of Food Chemistry and Technology, Greece

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ABSTRACT

The objective of this study was to investigate the effect of variable storage conditions on shelf life and quality characteristics of frozen shrimp. Colour change measured both instrumentally and visually was modelled by apparent zero order equations and showed high dependence on temperature. TVB-N and TMA values increased with storage time and were modelled with apparent first order equations. Taste and overall acceptability scores of frozen shrimp had high correlation with TVB-N and TMA values. The temperature dependence of quality deterioration was adequately modelled by the Arrhenius equation and activation energy ranged from 118 to 156 kJ/mol for the different indices measured. The developed models were validated in fluctuating time–temperature conditions in order to establish their applicability in the real cold chain.

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1. Introduction

The purpose of frozen storage of seafood is to extend its shelf life and to limit microbial and enzymatic activity which causes deterioration (Makarios-Laham & Lee, 1993). Shrimp is the most important seafood traded worldwide (Oosterveer, 2006). Frozen shrimp is a product of high commercial value and increasing demand, due to its competitive price and extended shelf life. Storage temperature and variability determines shelf life loss rates and final quality at the time of consumption or use. Since storage temperatures for shrimp in commercial handling and distribution vary (Shamshad, Kher-Un-Nisa, Riaz, Zuberi, & Qadri, 1990), it is important to be able to reliably estimate the effect on shelf life of any set of variable temperature conditions that have or are likely to occur in the actual frozen food chain.

The most important quality changes occurring during storage of frozen shrimp are colour fading (Chandrasekaran, 1994; Ghosh & Nerkar, 1991), lipid oxidation (Bottino, Lilly, & Finne, 1979; Reddy, Nip, & Tang, 1981; Riaz & Qadri, 1990), denaturation of protein (Bhobe & Pai, 1986); sublimation and recrystallization of ice (Londahl, 1997). These can result in off-flavours, rancidity, dehydration, weight loss, loss of juiciness, drip loss, textural changes (Bhobe & Pai, 1986; Gates, Eudaly, Parker, & Pittman, 1985; Londahl, 1997; Watabe & Hashimoto, 1987; Yamagata & Low, 1995), increase in volatile basic nitrogen (Riaz & Qadri, 1990; Yamagata & Low, 1995)

and reduced water binding capacity, as well as microbial spoilage and autolysis (Bhobe & Pai, 1986). The highest shrimp quality can be obtained in shrimp frozen immediately after harvest (Fennema, Karel, & Lund, 1975).

Overall quality and shelf life of whole frozen shrimp is the composite result of the above concurrently occurring actions the rates of which depend on storage temperature. It is important to prevent temperature fluctuations during transportation and storage, and to avoid thawing and re-freezing, to maintain the quality of frozen shrimp (Boonsumrej, Chaiwanichsiri, Tantratian, Suzuki, & Takai, 2007). Published information on systematic modelling of the temperature dependence and validation in variable conditions relevant to real cold chain conditions would be important for shelf life optimization and improvement of the cold chain management (Barroso, Careche, & Borderias, 1998; Laguerre & Flick, 2007; Nielsen & Jorgensen, 2004).

The objective of this study was to investigate and model the effect of variable storage conditions on shelf life and quality characteristics of frozen shrimp and demonstrate the applicability of the models in the cold chain.

2. Materials and methods

2.1. Raw material

Samples of whole frozen shrimp (size: 5 – origin: Atlantic ocean, Easter central, FAO 34) were obtained directly from the packer. Shrimp was provided by a vertically operated company that owns and operates both the fishing boats and the packing and storage facilities. After catch, shrimp was put into ice, treated with sulfites, size sorted and then quick frozen at $-40\text{ }^{\circ}\text{C}$. Then it was stored at

* Corresponding author. School of Chemical Engineering, Laboratory of Food Chemistry and Technology, National Technical University of Athens (NTUA), 5, Iroon Polytechniou, Zografou 15780, Athens, Greece. Tel.: +30 210 772 3171; fax: +30 210 772 3163.

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

–18 °C for 20 days until packing. All shrimp came from the same frozen batch and were packed in their usual commercial packages (cardboard lined with HDPE film, net weight: 425 g, dimensions: 20 × 16 × 5 cm). Then they were transported frozen (at constant –18 °C monitored with electronic, programmable miniature dataloggers – COX TRACER®, Belmont, NC) to the laboratory. Sixty packages in total were distributed and stored at controlled temperature cabinets (Sanyo MIR 553, Sanyo Electric Co, Ora-Gun, Gunma, Japan) at constant temperatures (–5, –8, –12 and –15 °C). Controls were stored at –30 °C. Measurements of selected quality indices were conducted with time during a 12 month period and data were analyzed and modelled.

In order to validate the applicability of the shelf life models from the isothermal experiments to real conditions, a variable temperature experiment was carried out. A time–temperature scenario (Var) was applied, consisting of repeated cycles of three successive temperature steps of –12 °C for 24 h, –5 °C for 36 h and –8 °C for 24 h in temperature programmable control cabinet (Sanyo MIR 153, Sanyo Electric Co, Ova-Gun, Gunma, Japan) corresponding to an equivalent effective temperature (T_{eff}) of –7.3 °C.

Temperature in the incubators and of the samples 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 quality deterioration. One package (425 g n.w.) was thawed at room temperature and sufficient quantities as described in the following sections, were used for analyses. Overall most of the single pack quantity was used. Samples were analyzed immediately after thawing. All determinations were made in duplicate samples.

2.2. Colour measurement

Quantification of the colour change was based on measurement of CIELab values (L-value: lightness, a-value: redness and greenness, b-value: yellowness and blueness), using a CR-Minolta Chromameter® (Minolta Co., Chuo-Ku, Osaka, Japan) with an 8 mm measuring area. The instrument was standardized under “C” illuminant condition according to the CIE (Commission Internationale de l’Eclairage) using a standard white reference tile (calibration plate CR-200, $L = 97.50$, $a = -0.31$, $b = -3.83$).

At predetermined times of storage, according to the design, measurements were conducted for shell and shrimp flesh at two points. All measurements were carried out on three different single shrimp specimens. The average values were reported and values of ΔC and ΔE were determined:

$$\Delta C = \sqrt{(a - a_0)^2 + (b - b_0)^2} \quad (1)$$

$$\Delta E = \sqrt{(L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2} \quad (2)$$

where L_0 , a_0 , and b_0 are the values of L , a and b colour parameters at storage time zero.

2.3. Texture measurement

Mechanical properties were measured using a compression test to thawed peeled shrimp with a texture analyzer (MODEL TA-XT2i, Stable Micro Systems, Godalming, Surrey, United Kingdom). A flat-ended cylinder of 20 mm diameter was selected to simulate the human finger. Constant penetration depth was applied on the shrimp flesh and penetration depth of 2 mm was selected as the maximum distance which could be applied without affecting the muscle

structure by erupting and leaving a mark on the shrimp flesh. Double compression was applied to construct the texture profile analysis (TPA) parameters of three different specimens. The flat-ended cylinder approached the sample at the speed of 0.5 mm/s and penetrated 2 mm into the shrimp flesh. Then the force was reduced and the sample was allowed to rebound 5 s. Then the cylinder was pressed on the sample a second time, force–distance curves were obtained and texture parameters (hardness, elasticity, cohesiveness, adhesiveness, gumminess, chewiness) were determined (Sigurgisladdottir et al., 1999).

2.4. Microbiological analysis

Representative sample (10 g) was transferred to a sterile stomacher bag with 90 mL sterilized Ringer solution (Merck Ringer Tablets in distilled water) and was homogenized for 60 s with a Stomacher (BagMixer® interscience, France).

Samples (0.1 mL) of 10-fold serial dilutions of shrimp homogenates were spread on the surface of the appropriate media (Plate Count Agar – PCA, Merck) in Petri dishes for enumeration of total aerobic viable count and incubated at 25 °C for 72 h. Two replicates of at least three appropriate dilutions were enumerated. All plates were examined visually for typical colony types (Koutsoumanis, Giannakourou, Taoukis, & Nychas, 2002). Isolated cultures were characterized by microscopy, Gram stain, catalase and oxidase reactions. Isolates obtained from the samples were identified using the API 20NE method (Bio-Mérieux, Marcy L’Etoile, France). Preparation of samples, inoculations and interpretation of reactions were carried out according to the manufacturer’s instructions.

2.5. pH measurement

Representative sample of shrimp flesh (10 g) was transferred to a stomacher bag with 90 mL Ringer solution and was homogenized for 60 s with a Stomacher. The pH of this homogenized sample was measured using a pHmeter (Amel Instruments 338 pHmeter).

2.6. Measurements of chemical indices

2-Thiobarbituric acid reactive substances (TBARS) assay, to evaluate lipid oxidation, was performed according to the method of Loovas (Loovas, 1992). Sample 5 g was homogenized in 15 mL distilled water. One mL of homogenized sample was dispersed in 2 mL of thiobarbituric acid (TBA) solution (15 g trichloroacetic acid [TCA], 0.375 g TBA, 1.76 mL HCl 12 N, 82.9 mL H₂O). The mixture was set in boiling water bath for 15 min and after cooling it was centrifuged at 2000 g for 15 min. The absorbance was measured at 532 nm with a digital spectrophotometer (Unicam Helios, Spectronic Unicam EMEA, Cambridge, United Kingdom).

Total volatile basic nitrogen (TVB-N) and trimethylamine nitrogen (TMA-N) analyses were conducted on a single TCA extraction by distillation in a Kjeldhal rapid distillation unit (Büchi 321 Distillation unit, Flawwil, Switzerland) and titration with sulphuric acid (Pivarnik, Ellis, Wang, & Reilly, 2001).

2.7. Sensory analysis

The sensory attributes of raw and cooked shrimp were evaluated by a sensory panel of eight, selected according to ISO 8586 and trained using discriminative tests with practice evaluation methods of determining spoilage characteristics in shrimp (Botta, 1995). Thawed shrimp were cooked in boiling water for 3 min. Panellists were asked to score appearance and odour of raw unpeeled and peeled shrimp and appearance, odour, texture, taste and overall acceptability of cooked shrimp, in appropriate forms with descriptive terms reflecting the organoleptic evolution of quality

deterioration. Rating was assigned separately for each parameter on a 1–9 descriptive hedonic scale (9 being the highest quality score and 1 the lowest). A score of 5 of sensory acceptability was taken as the average score for minimum acceptability.

2.8. Data analysis

Values of the different measured indices were plotted vs. time for all temperatures studied and the apparent order of quality loss was determined based on the least square statistical fit. The temperature dependence of the deterioration rate constant, k , was then modelled by the Arrhenius equation (3):

$$\ln k = \ln k_{\text{ref}} - \left(\frac{E_a}{R} \right) \left[\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right] \quad (3)$$

where k_{ref} is the rate constant of the degradation of the respective quality index at a reference temperature, T_{ref} (-18°C for frozen foods), T is the temperature in K, E_a is the activation energy of the studied action and R is the universal gas constant. The activation energy (E_a) values were estimated from the slope of Arrhenius plots of $\ln k$ vs. $(1/T_{\text{ref}} - 1/T)$, by linear regression (Fu & Labuza, 1997; Giannakourou & Taoukis, 2003a).

3. Results

3.1. Effect of frozen storage on appearance and colour

At zero storage time shrimp had a very translucent and shiny body. Samples stored at -5 and -8°C developed severe blackening in the head and gill regions after 1 and 3 months of storage respectively, and consequently had a poor appearance and were unacceptable. All samples stored at -12 and -15°C had acceptable appearance, as judged by the sensory panellists, for approximately 8 and 11 months of storage, respectively.

Colour was also quantified by instrumental measurement. The b -value of thawed, unpeeled samples showed a pronounced increase at highest storage temperatures as shown at Fig. 1a, and was a good quality index. The change of b -value of shrimp shell during frozen storage was found to be adequately modelled by an apparent zero order reaction:

$$b = k_b t + b_0 \quad (4)$$

where k_b is the colour change rate constant at temperature T , and b , b_0 the values at storage times t and zero, respectively.

The sensory scores of colour of thawed unpeeled shrimp correlated well to instrumental measured changes, as shown in Fig. 1b. Colour sensory scores were adequately modelled by an apparent zero order reaction:

$$s = -k_s t + s_0 \quad (5)$$

where k_s is the colour change rate constant at temperature t and s , s_0 the sensory scores of colour at storage times t and zero, respectively. The instrumental and sensory colour changes were linearly correlated:

$$s = -1.08 b + 13.34, \quad R^2 = 0.902 \quad (6)$$

The colour degradation rates were high for the higher storage temperatures (-5 and -8°C), where samples showed noticeable enzymatic blackening. Temperature dependence of the rates of colour degradation was adequately described by Arrhenius kinetics in the temperature range studied, as shown in Fig. 2. Changes of b -value and sensory colour scores had high E_a values, 156 ± 9 kJ/mol ($R^2 = 0.994$) and 143 ± 15 kJ/mol ($R^2 = 0.979$), respectively, 95%

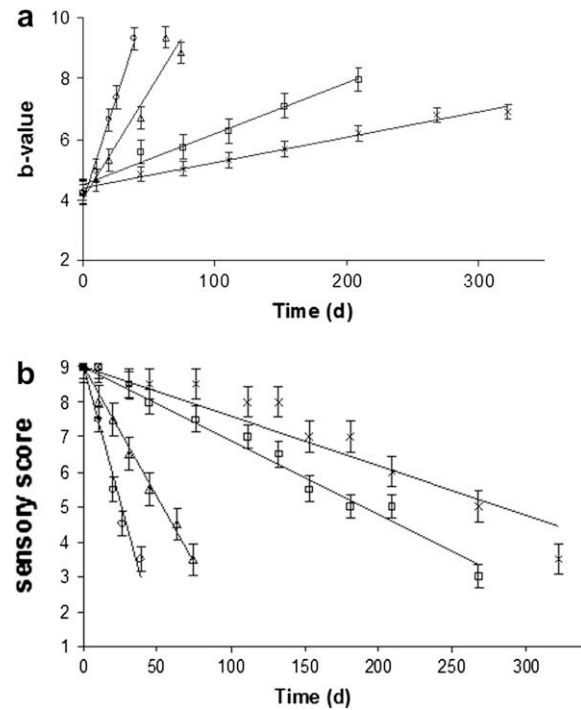


Fig. 1. (a) Changes of colour (b -value) of thawed non-peeled frozen shrimp, (b) Sensory scores for colour of thawed non-peeled frozen shrimp during storage at \circ : -5°C , Δ : -8°C , \square : -12°C and $*$: -15°C . (Error bars indicate standard error of measurements of two different samples.)

confidence intervals based on the statistical variation of the kinetic parameters of the Arrhenius model – regression analysis, indicating the same strong dependence on storage temperature.

3.2. Effect of frozen storage on texture

At zero storage time thawed shrimp was firm and elastic in texture. Texture parameter changes occurred but were not significantly dependent on time and temperature. Samples became mushy and with a chewy texture during storage at -5°C . At lower storage temperatures shrimp flesh developed a dry, rigid texture.

Hardness and elasticity recorded by texture analysis during frozen storage are shown in Fig. 3a, b, respectively, and showed decreasing values at higher storage temperatures but small changes, within sample variability, for shrimp stored at -12 and -15°C . Yamagata and Low (1995) reported that the texture of frozen shrimp changed from firm to soft after 7 weeks at -10°C . They also reported that samples stored at -20°C had slightly softer texture

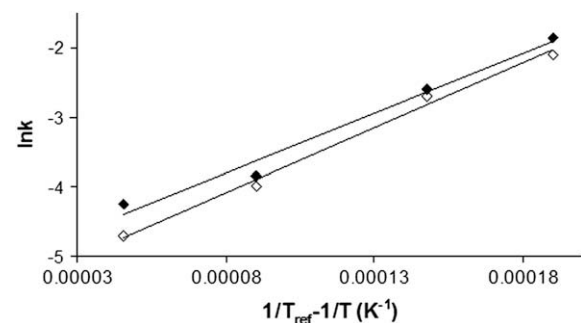


Fig. 2. Effect of temperature on colour change rates of thawed non-peeled frozen shrimp, measured \diamond : instrumentally (b -value, $E_a = 156$ kJ/mol, $k_{\text{ref}(T_{\text{ref}} = -18^\circ\text{C})} = 0.0037$ day $^{-1}$) and \blacklozenge : by sensory analysis ($E_a = 143$ kJ/mol, $k_{\text{ref}(T_{\text{ref}} = -18^\circ\text{C})} = 0.0056$ day $^{-1}$), during storage.

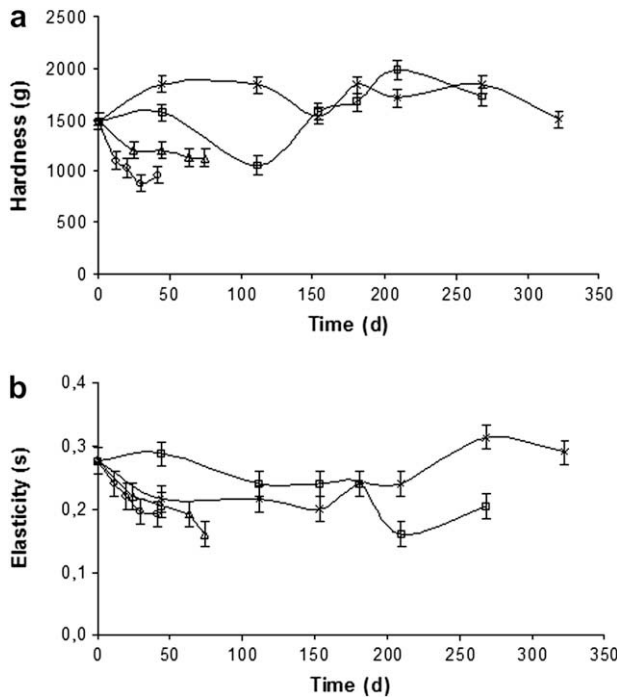


Fig. 3. Effect of temperature on texture parameters: (a) hardness and (b) elasticity of thawed peeled frozen shrimp, measured instrumentally during storage at \circ : $-5\text{ }^{\circ}\text{C}$, Δ : $-8\text{ }^{\circ}\text{C}$, \square : $-12\text{ }^{\circ}\text{C}$ and $*$: $-15\text{ }^{\circ}\text{C}$. (Error bars indicate standard error of measurements of two different samples.)

after 6 months. Other texture parameters measured (cohesiveness, adhesiveness, gumminess and chewiness) showed small changes, within sample variability, during storage at all temperatures. Thus, texture parameters changes were not modelable indices of quality deterioration.

3.3. Effect of frozen storage on microbial growth

Thawed shrimp samples showed initially total viable count of 5.7 log CFU/g . This value is higher than the ones reported by Hatha, Paul, and Rao (1998) who found initial aerobic plate count in the range of 10^4 in most of the frozen shrimp samples, indicating good sanitary practices followed in the processing unit under study. Nevertheless, there are reported initial values of 10^6 log CFU/g for warm water marine shrimp (Jeyasekaran, Ganesan, Anandaraj, Jeya Shakila, & Sukumar, 2006). Vanderzant, Cobb, Thompson, and Parker (1973) reported that warm water marine shrimp often showed total aerobic counts of 10^6 CFU/g when captured. Slow microbial growth was measurable at -5 and $-8\text{ }^{\circ}\text{C}$, as shown in Fig. 4a. This slow growth at near subfreezing temperatures was confirmed with an additional independent experiment. In both experiments no change in counts was measured at temperatures lower than $-8\text{ }^{\circ}\text{C}$. Examination of the obtained colonies showed mainly Gram-negative, oxidase and catalase-positive, coccobacilli shaped cells. According to the API test, isolates were classified with a 91% confidence as *Psychrobacter phenylpyruvicus*. Bacteria of the genus *Psychrobacter* are halo- and psychrotolerant (some species are psychrophilic), with wide distribution in marine environments and association with seafood (Onishchenko & Kiprianova, 2004). According to Makarios-Laham and Lee (1993), psychrophilic microorganisms, contaminants from the natural environment, may contribute to deterioration of seafoods during frozen storage.

In the present study, despite the apparent increase in total viable count, the samples were not judged as “spoiled” by the sensory panel.

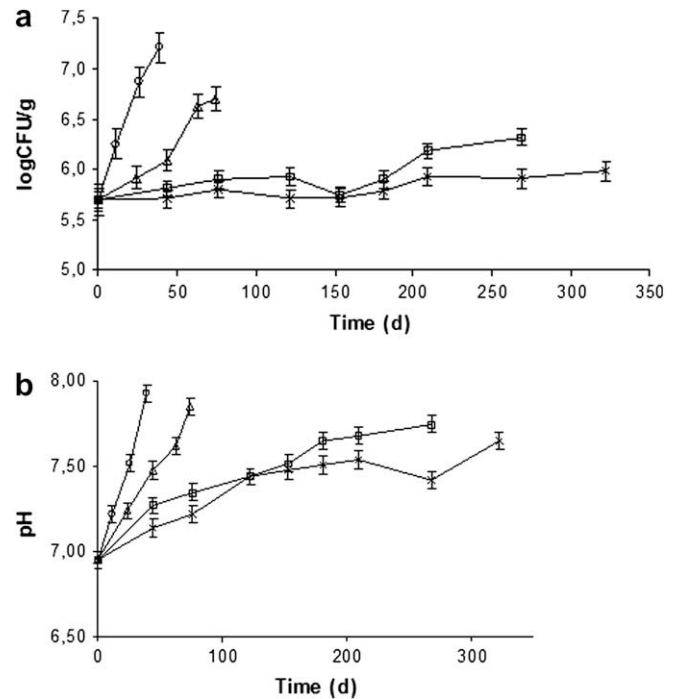


Fig. 4. (a) Growth of total viable count and (b) pH changes of frozen shrimp during storage at \circ : $-5\text{ }^{\circ}\text{C}$, Δ : $-8\text{ }^{\circ}\text{C}$, \square : $-12\text{ }^{\circ}\text{C}$ and $*$: $-15\text{ }^{\circ}\text{C}$. (Error bars indicate standard error of measurements of two different samples.)

3.4. Effect of frozen storage on pH

pH increased with time and temperature due to biochemical reactions (Shamshad et al., 1990). The initial pH of 6.95 increased to pH 7.93 and 7.85 after 39 and 74 days at -5 and $-8\text{ }^{\circ}\text{C}$, respectively, as shown at Fig. 4b.

3.5. Effect of frozen storage on lipid oxidation

Storage at -5 and $-8\text{ }^{\circ}\text{C}$ resulted in pronounced lipid oxidation as shown at Fig. 5. For samples stored at -12 and $-15\text{ }^{\circ}\text{C}$ a smaller but significant increase was seen after 3.5 and 9 months, respectively. Bak, Andersen, Andersen, and Bertelsen (1999) reported significant lipid oxidation during frozen storage of shrimp in atmospheric air. Due to the fact that the increase of the TBARS values was followed by a decrease at all temperatures, this measurement could not be used as a consistent quality index for the whole shelf life.

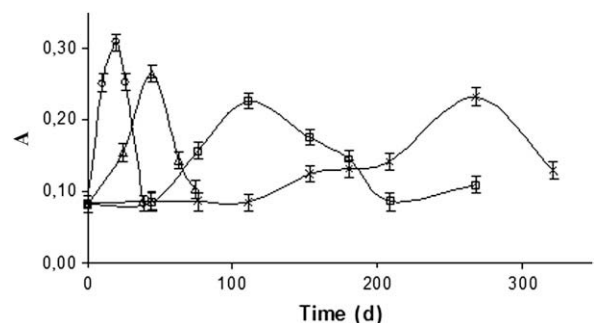


Fig. 5. Change of absorbance by TBARS method as a measure of lipid oxidation of frozen shrimp during storage at \circ : $-5\text{ }^{\circ}\text{C}$, Δ : $-8\text{ }^{\circ}\text{C}$, \square : $-12\text{ }^{\circ}\text{C}$ and $*$: $-15\text{ }^{\circ}\text{C}$. (Error bars indicate standard error of measurements of two different samples.)

3.6. Effect of frozen storage on TVB-N and TMA-N

Changes in TVB-N and TMA-N values are presented in Fig. 6a, b. TVB-N and TMA-N contents were initially 6.49 and 2.85 mg N/100 g and increased with storage time up to approximately 25 and 14 mg N/100 g, respectively, at the end of storage time. TVB-N and TMA-N values were modelled with apparent first order equations as shown in Eq. 7 ($R^2 > 0.90$ for all experiments):

$$\frac{A}{A_0} = e^{kt} \quad (7)$$

where k the kinetic rate at temperature T and A , A_0 the values of TVB-N or TMA-N at storage times t and zero, respectively.

The production of TVB-N followed a pattern similar to that of TMA-N. Temperature dependence of the rates of the production of TVB-N and TMA-N was adequately described by Arrhenius kinetics (R^2 0.981 and 0.977, respectively) in the temperature range studied (Fig. 7) and was practically the same, as was determined by the activation energy, E_a , values of 119 ± 13 and 118 ± 12 kJ/mol, respectively (95% confidence intervals based on the statistical variation of the kinetic parameters of the Arrhenius model – regression analysis). These values were lower than the respective for colour change, indicating a smaller temperature dependence of the chemical indices. The increase in TMA at the higher storage temperatures of -5 and -8 °C was in line with the slow microbial growth observed in this temperature range. A pronounced increase in TMA production was observed by López-Caballero, Gonçalves, and Nunes (2002) after 9 days of storage in aerobically iced stored shrimp, when total bacteria count were about 5–7 log CFU/g. Sarma (1998) reported that TVN and TMA in pink perch and sardine stored at freezing temperatures increased significantly. Kodrala (1996) reported a high increase of TVN in shrimp (with head and tail) stored in ice and changes correlated also with the microbial flora.

The values of TVB-N and TMA-N were measured during non-isothermal experiments and were compared with the values predicted by integration of the models from the isothermal

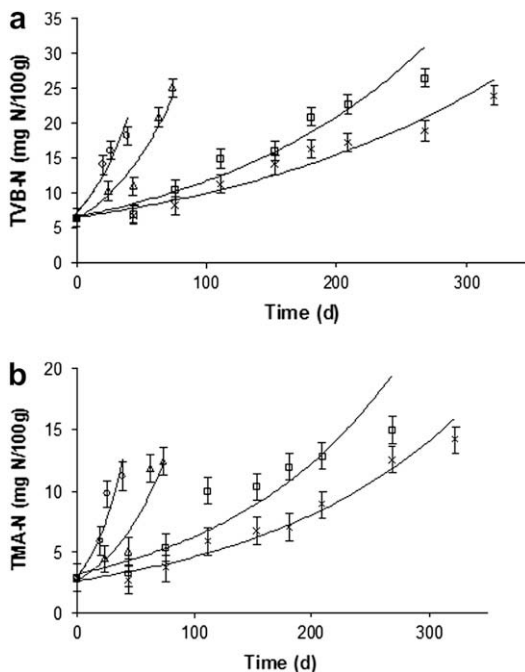


Fig. 6. Changes in (a) TVB-N and (b) in TMA-N of frozen shrimp during storage at \circ : -5 °C, Δ : -8 °C, \square : -12 °C and $*$: -15 °C. (Error bars indicate standard error of measurements of two different samples.)

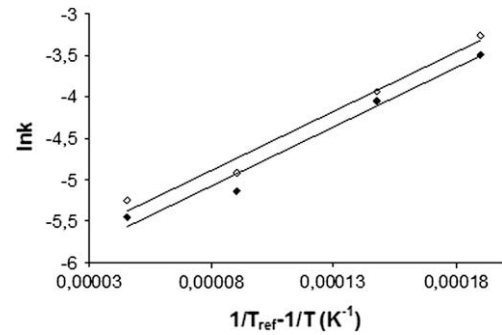


Fig. 7. Effect of temperature on rates of \blacklozenge : TVB-N ($E_a = 119$ kJ/mol, $k_{ref}(T_{ref} = -18$ °C) = 0.0020 day $^{-1}$) and \diamond : TMA-N ($E_a = 118$ kJ/mol, $k_{ref}(T_{ref} = -18$ °C) = 0.0024 day $^{-1}$) changes of frozen shrimp during storage.

experiments (Fig. 8), validating the applicability of the developed models at variable conditions.

3.7. Sensory evaluation

Sensory scores were determined by panellists and shelf life was determined using the average values. All indices (appearance, odour, taste, overall acceptability) showed decline with storage time and temperature. Taste and overall acceptability were considered as good quality indexes, as they were well correlated with chemical indices determined.

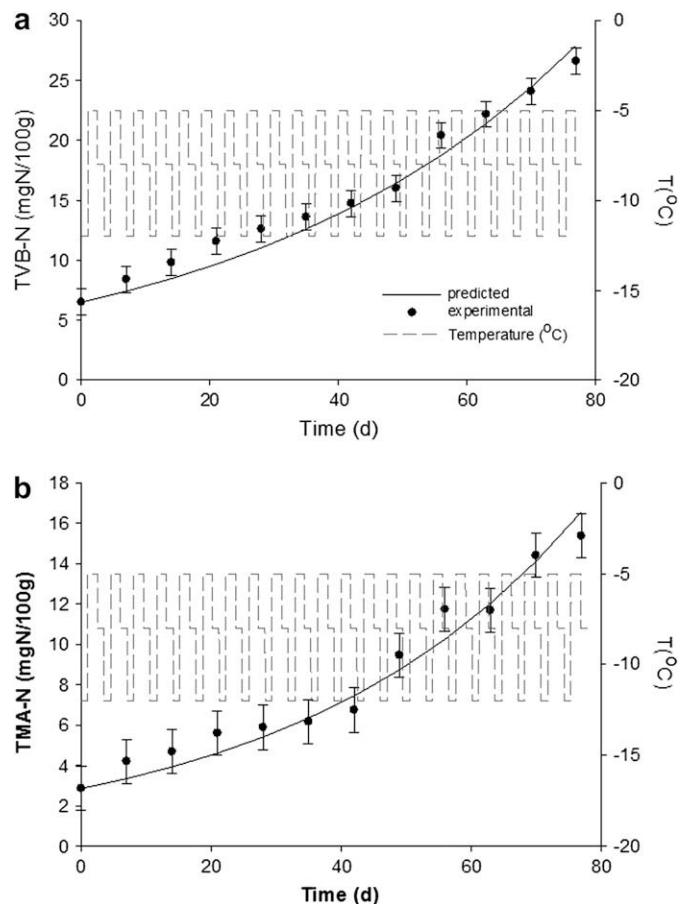


Fig. 8. Comparison of \bullet : experimental and — : predicted changes in (a) TVB-N and (b) TMA-N of frozen shrimp at the temperature profile (---) of the non-isothermal experiment ($T_{eff} = -7.3$ °C). (Error bars indicate the standard error of the predicted y-value for each x in the regression.)

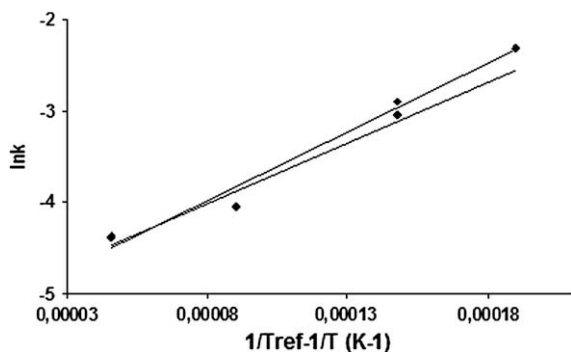


Fig. 9. Effect of temperature on \blacklozenge : taste ($E_a = 124 \text{ kJ/mol}$, $k_{\text{ref}(T_{\text{ref}}=-18^\circ\text{C})} = 0.0056 \text{ day}^{-1}$) and \diamond : overall acceptability ($E_a = 111 \text{ kJ/mol}$, $k_{\text{ref}(T_{\text{ref}}=-18^\circ\text{C})} = 0.0062 \text{ day}^{-1}$) of frozen shrimp determined by sensory evaluation during storage.

Sensory scorings of taste and overall acceptability were modelled by apparent zero order reactions and the results for temperature dependence were in agreement with the ones for chemical indices, showing similar E_a values of 124 ± 14 and $111 \pm 24 \text{ kJ/mol}$, respectively (Fig. 9) (95% confidence intervals based on the statistical variation of the kinetic parameters of the Arrhenius model – regression analysis).

The shelf life of frozen shrimp determined based on TVB-N values and sensory scoring is shown on Table 1.

The results of the sensory evaluation (taste and overall acceptability scores) of frozen shrimp stored at non-isothermal conditions are presented in Fig. 10a, b. Overall, the results showed a satisfactory agreement between the experimental points and the prediction based on the kinetic model established. The agreement of the experimental measurements of chemical indices and sensory scores with predictions from the developed models supports the assumption that they can be applied reliably in the dynamic temperature conditions of the real chill chain.

4. Discussion

The aim of the present study was to establish and validate reliable kinetic models of different quality indices for frozen shrimp during frozen storage that would allow estimation of the quality of frozen shrimp during non-isothermal handling of products, in the real distribution path of frozen foods. The different indices examined are all relevant to the gradual deterioration of colour, texture and flavour that becomes evident organoleptically during prolonged storage of frozen shrimp. These included instrumental measurements of colour and texture, evaluation of rancidity, protein degradation and off-flavours by chemical measurements (TBARS, TVB-N and TMA-N), and sensory scoring by a trained panel. The indices that could more consistently be correlated to time-temperature history of the products were instrumentally measured colour (b -value), chemical indices TVB-N and TMA-N and sensory scores. Slow microbial growth was measurable only at the higher temperatures and unlike respective studies for chilled foods

Table 1
Shelf life of frozen shrimp stored at -5 , -8 , -12 , -15 and -18°C

Storage temperature ($^\circ\text{C}$)	Shelf life of frozen shrimp (days)	
	Sensory scoring (limit = 5)	TVB-N (limit = 25 mgN/100 g)
-5	51	45
-8	90	82
-12	194	187
-15	351	353
-18	644 ^a	677 ^a

^a Calculated using the models developed.

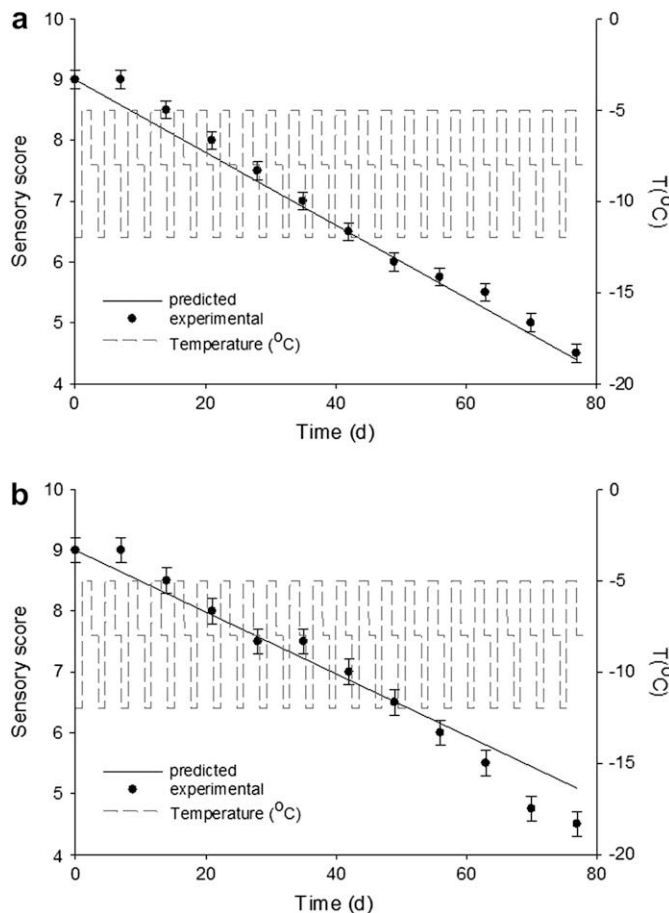


Fig. 10. Comparison of \bullet : experimental and — : predicted scores of (a) taste and (b) overall acceptability of frozen shrimp at the temperature profile (---) of the non-isothermal experiment ($T_{\text{ref}} = -7.3^\circ\text{C}$). (Error bars indicate the standard error of the predicted y-value for each x in the regression.)

(Koutsoumanis & Nychas, 2000) it could not be correlated to spoilage observable and scored by the sensory panel. TBARS increased with storage but decreased again after a level of lipid oxidation and thus a single TBAR measurement cannot uniquely indicate the extent of oxidation. The enzymic discoloration was more temperature dependent (higher activation energy) than the chemical indices and hence the latter will determine acceptability if lower temperature storage conditions prevail, whereas colour change will be the dominant reason for rejection at inadequate storage of -10°C or higher. As indicated by the experiments at the variable conditions, the rates of change of the indices are not

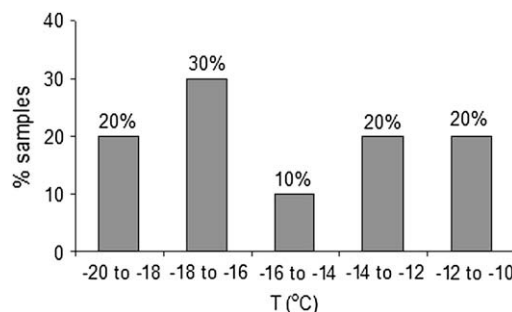


Fig. 11. Average storage temperatures measured in different types of retail freezers in several stores of a large supermarket chain.

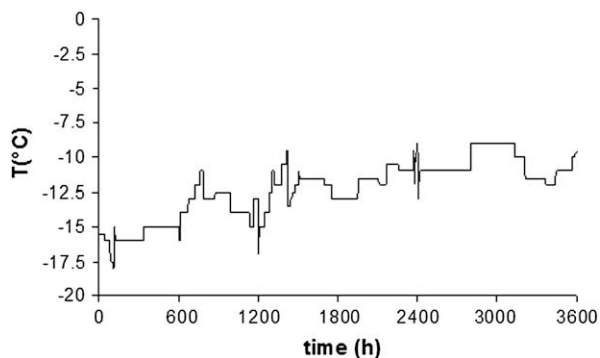


Fig. 12. Indicative temperature profile of distribution of frozen shrimp in the real chill chain – total distribution time 150 days – (first stage: packing plant storage, second stage: transportation–distribution center, third stage: retail storage, fourth stage: domestic storage).

dependent on the temperature history. Of course the starting value of any indice will affect the time to reach the upper acceptable level, i.e., shelf life, and this parameter can be taken into account in the developed models.

Periodic consumer complaints and regulatory actions confirm to the processors that the product that reaches the consumer is often not of the same quality as the one leaving their manufacturing facilities (Gates et al., 1985). It has been reported that a substantial portion of frozen products are exposed, throughout the distribution, including retail and domestic storage, to effective temperatures that deviated significantly from the recommended range (Giannakourou & Taoukis, 2003b; Giannakourou, Taoukis, & Nychas, 2006). Temperature data from recent surveys conducted by our laboratory in collaboration with a leading supermarket chain are illustrated in Fig. 11. The obtained results, although relatively improved compared to the above reported, showed that, despite the good practices and monitoring and control efforts, significant temperature fluctuations were observed during retail storage in the different types of freezers. Namely, products stored in the upper shelves of horizontal freezers were often exposed to temperatures close to -10°C , whereas only in the lowest shelves the recommended storage temperatures were recorded. The deviations in the domestic storage remained even more pronounced, with recorded temperatures as high as -5°C , in certain cases (unpublished results).

To demonstrate the applicability of the developed models, a realistic distribution scenario (Fig. 12) in the current chill chain is simulated. It includes an initial stage of 25 days storage in the packing plant, followed by transportation and storage in a distribution center for 25 days. Subsequently, shrimp are kept at retail freezers for 50 days, before being purchased by the final consumers that store them in their domestic freezer for 50 days before cooking

Table 2
Quality deterioration and remaining shelf life according to different quality indexes of frozen shrimp at the end of each stage of the distribution cycle

	First stage $T_{\text{eff}} \approx -15.6^{\circ}\text{C}$ duration: 25 day	Second stage $T_{\text{eff}} \approx -13.2^{\circ}\text{C}$ duration: 25 day	Third stage $T_{\text{eff}} \approx -11.8^{\circ}\text{C}$ duration: 50 day	Fourth stage $T_{\text{eff}} \approx -10.4^{\circ}\text{C}$ duration: 50 day
TVB-N (mgN/ 100 g)	7.07	8.13	11.9	19.6
Sensory scoring	8.75	8.34	7.26	5.86
Remaining shelf life (day): $T_{\text{ref}} = -15^{\circ}\text{C}$	329	294	197	69

and consumption. The extent of quality deterioration at the end of each distribution phase was estimated (Table 2). At the end of the assumed cycle, i.e., the time of consumption, the remaining shelf life of shrimp (at -15°C) according to TVB-N value and sensory acceptability was approximately 70 days. The nominal remaining shelf life based on the “use by” date, which does not consider the time–temperature history of the products would be more than 200 days.

If the temperature conditions of the products could be continuously monitored, e.g., by inexpensive Time–Temperature Integrators, reliable estimation of the quality status and the remaining shelf life of the products could be performed based on the presented modelling of the quality indices. This could allow better management and optimization of the cold chain (Giannakourou et al., 2006), from manufacture to consumption.

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