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# Simulated real-time shelf life of frozen yellowfin tuna and Argentine hake products

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By Ilenia Dottori , Stefania Urbani , Luigi Daidone , Arianna Bonucci , Matteo Beccerica , Roberto Selvaggini , Beatrice Sordini , Raffaella Branciarì , Gianluca Veneziani , Davide Nucciarelli , Agnese Taticchi , Maurizio Servili and Sonia Esposto

## Study focuses on impacts of light and oxygen on frozen and glazed fish products over time



Study simulates real-time shelf life of frozen products of yellowfin tuna and Argentine hake. Results showed that the different composition of these fishes affects their conservation after the freezing process and improved it by glazing in the case of the hake fillets. Photo of yellowfin tuna school by Marc Taquet (CC BY 4.0, <https://creativecommons.org/licenses/by/4.0>, via Wikimedia Commons).

Once a fish has been caught, deterioration starts very quickly, with rigor mortis being the main culprit. At this stage, the metabolic activity of microorganisms and endogenous enzymes (autolysis) and the chemical oxidation of lipids lead to the degradation of chemical components and the formation of new ones, which are **responsible for changes** (<https://doi.org/10.3390/foods10040780>), in safety and sensory quality. **Lipid oxidation** (<https://doi.org/10.1590/fst.32518>) is one of the main processes causing the quality deterioration of fish products, promoting free radical accumulation and rancidity.

Microbial development is the main mechanism of the oxidative deterioration of fish, with lipids being oxidized by both enzymatic and non-enzymatic means. Fish fats are more susceptible to oxidation, both because of their higher content of polyunsaturated fatty acids and due to rapid microbial growth. Refrigeration, deep-freezing and freezing techniques allow for fish to be stored for relatively longer periods without significant changes in quality. However, lipid oxidation does not stop during frozen storage, and refrigeration (storage at 0–4 degrees-C) **cannot guarantee long preservation times** (<https://doi.org/10.3390/foods11081100>) for fish. **Super-freezing** (<https://doi.org/10.3390/foods9121739>), adopting temperatures between refrigeration and freezing, allows for the freezing of only 5–30 percent of the water contained.

With freezing, all microorganisms cease developing but can still remain in a dormant state. Indeed, freezing has a bacteriostatic effect. To allow for further flesh preservation, glazing is carried out, covering the frozen products with a thin layer of ice (usually ranging between 5 and 15, and up to 50 percent of the fish weight). The potential and unique advantage of ice coating is its ability to exclude air from the surface of the product, preventing oxidation and thus extending the shelf life of the food.

Another advantage of this technology is that it is not expensive. In conclusion, the combination of freezing and glazing with ice is currently among the most extensively used methods for preserving fish and fish products in their natural state.

This article – **summarized** (<https://doi.org/10.3390/foods14081334>) from the **original publication** (<https://creativecommons.org/licenses/by/4.0/>). (Dottori, I. et al. 2025. A Simulation of the Real-Time Shelf Life of Frozen Fish Products in a Bulk System Sale. *Foods* 2025, 14(8), 1334) – reports on a study that simulated the real-time shelf life of frozen fillets of two different types of fish, yellowfin tuna and Argentinian hake.



(<https://info.globalseafood.org/get-certified>).

## Study setup

To fully assess the effect of these conditions, an ordinary sales condition of unpackaged fishes was simulated using two very different types of fish in terms of lipid contents: yellowfin tuna (*Thunnus albacares*, cut into slices) and Argentine hake (*Merluccius hubbsi*, cut into fillets) and simulating a bulk system sale.

A glaze treatment was used on all the samples at the beginning, and during the 60-day storage period, the glaze was reapplied at regular intervals on half of the samples ("glazed"), while the other half was not re-glazed ("control"). To assess the quality changes in the two products, the peroxide value (PV), total volatile basic nitrogen (TVB-N), biogenic amines and volatile composition were determined every twenty days.

For detailed information on the experimental design, fish samples, storage conditions, and sample collection and analyses, refer to the original publication.



## How aging uncertainty of major tuna species impacts the estimation of growth functions

Aging error and age range influences the uncertainty of growth estimation in major tuna species, necessitating improved accuracy of age analysis.



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## Results and discussion

Using multivariate statistical analysis, it was possible to distinguish between the samples of hake and tuna according to their storage time, as well as the different treatments that they underwent (with or without reapplication of the glaze).

The Principal Component Analysis (PCA; a technique used to emphasize variation and bring out strong patterns in a dataset) applied to the results of our analysis of the hake samples (Fig. 1) explained 93 percent of the total variance with three significant principal components (explaining 80, 8 and 5 percent, respectively). The relative score plot of the first two principal components shows a separation of the samples according to the time of storage along the first component (from the left to the right side of the score plot) and a differentiation of the fillets according to the treatment (glazed vs. control) along the second component (from the lower to the upper side of the score plot). The glazed ice layer excludes air from the surface of the product, thus reducing the rate of oxidation.

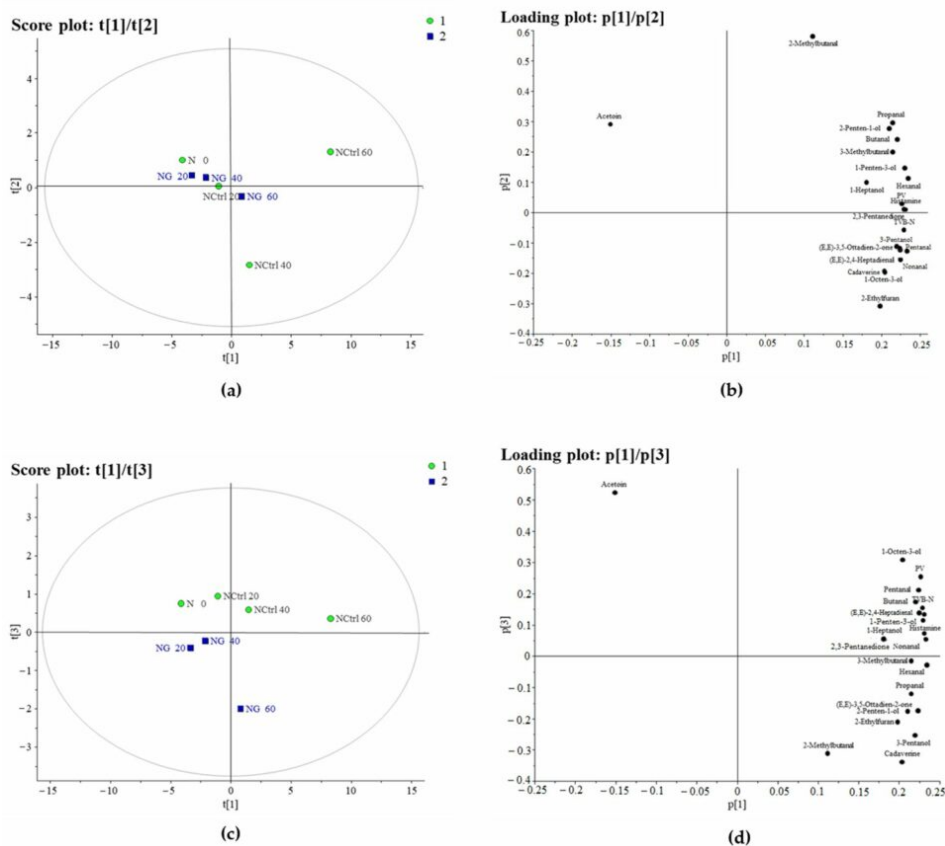


Fig. 1:(a) Score (t1/t2) and (b) loading (p1/p2) plots of the first and second principal components (explaining 80 and 8 percent, respectively) of the PCA model, constructed using the hake samples. (c) Score (t1/t3) and (d) loading (p1/p3) plots of the first and third principal components (explaining 80 and 5 percent, respectively) of the PCA model, constructed using the hake samples. Green dots represent control samples, while blue squares represent glazed samples.

The PCA model for tuna (Fig. 2) explains 95 percent of the total variance, with three significant principal components (each explaining 80, 8 and 7 percent, respectively). The score plot of the first and second principal components showed a distribution of the samples according to conservation (from the left to the right side of the score plot), irrespective of the treatment that they underwent. As the duration of storage increased, the content of several compounds related to fish decomposition increased.

Fig. 2: (a) Score (t1/t2) and (b) loading (p1/p2) plots of the first and second principal components (explaining 80 and 8 percent, respectively) of the PCA model, constructed using the tuna samples. (c) Score (t1/t3) and (d) loading (p1/p3) plots of the first and third principal components (explaining 80 and 7 percent, respectively) of the PCA model, constructed using the tuna samples. Green dots represent control samples, while blue squares represent glazed samples.

Overall, these preliminary results suggest that the glazing process, in addition to temperature and storage time, could positively influence the quality characteristics of both fish throughout their shelf life. Further analyses were therefore conducted in order to assess the development of several parameters.

The peroxide value is a parameter for determining the degree of lipid oxidation, including in fish products. During the storage of a frozen product, lipid oxidation proceeds more slowly, and therefore, fewer oxidation products are formed. In fish, this also depends on the initial lipid content, temperature and length of the storage period. Peroxides are used to measure the primary products of lipid oxidation, in particular, hydroperoxides. They undergo decomposition by reducing the peroxide value and generating a wide variety of aldehyde control molecules.

Our analysis showed an increase in these molecules during exposure to the tested products. The peroxide value first increased significantly in both fishes but after 40 days of storage, it decreased significantly in the tuna, indicating the production of secondary oxidation compounds. In the hake, after 60 days, there was a significant difference between the glazed and control samples. In contrast, there

was no significant difference in the tuna, probably as a consequence of the thick initial glazing layer (20 percent) on the control samples, thus subjecting them to very similar exposure conditions to the glazed samples.

Total volatile basic nitrogen (TVB-N) is a spoilage index for determining the freshness of fish; the legal limit is 35 mg per 100 grams]. The production of TVB-N is related to the metabolism of spoilage bacteria and the activity of endogenous enzymes that cause the degradation of proteins and non-protein nitrogen compounds, generating volatile ammonia control compounds (NH<sub>3</sub>) and other compounds.

Both products, glazed and unrestored, did not exceed the legal limits for TVB-N (<35 mg per 100 grams) and histamine (<100 mg/kg) but remained far below these limits. The TVB-N content increased in both products but not significantly since microbial activity was inhibited at freezing temperatures. There were no significant differences between the glazed and control samples in both fishes. This could be attributed to the fact that in a frozen stored product, microbial and enzymatic activity are minimized. During frozen preservation, a decrease in fish freshness may occur due to slow microbial growth and enzyme activities in muscle tissues.

## Are alternative shelf life-extending protocols effective on seafood products?



Implementing additional treatments in seafood processing could reduce the need for freezing, extending the shelf life of fresh unfrozen products.



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Microbial activity is responsible for the production of **biogenic amines** ([https://doi.org/10.1007/978-1-4419-0826-1\\_1](https://doi.org/10.1007/978-1-4419-0826-1_1)), such as histamine, cadaverine, tyramine and putrescine. Some factors that influence microbial and enzymatic activity are temperature, pH, water activity and oxygen availability. The combination of these factors can be responsible for the variability of biogenic amine content. The prevention of biogenic amine formation in raw fish is mainly based on rapid chilling after catch and subsequent storage at ice-cold temperatures, as well as good handling and hygiene practices on board vessels. Ice, slurry ice or mechanically chilled seawater can be used to chill fish after harvesting. One of the most important biogenic amines is histamine, and in the EU the legal limit is 100 mg/kg.

Histamine was found in both fishes, while cadaverine was found in hake and spermidine in tuna. Biogenic amines, in particular histamine, increased significantly in both fishes during the 60-day trial. In particular, in the hake, there was a significant difference between the glazed and control samples. In tuna, the histamine levels were higher than in hake but there were no statistically significant differences between the control and glazed samples. The histamine values that were reached at the end of the trial were below the legal limit. The glaze played a fundamental role in inhibiting histamine formation. The

production of biogenic amines can be related to the composition of the fish flesh, which explains why the amines found in the two fish species evaluated here were not the same, except for histamine, which had very different values.

Volatile compounds can be generated by enzymatic reactions, lipid oxidation or microbial action. The action of microorganisms is irrelevant during storage at freezing temperature; however, freezing cannot prevent lipid oxidation, leading to the formation of volatile substances. The oxidation of lipids is commonly expressed by the peroxide value (PV) and thiobarbituric acid reactive substances (TBARS; formed as degradation products of fats). However, as peroxides decompose into oxidation by-products and TBARS are not specific, the evaluation of volatile compounds is a popular means of assessing lipid oxidation in hake. In general, the **main substances formed** (<https://doi.org/10.1016/j.fm.2018.01.011>) are aldehydes, esters, ketones and alcohols. Fig. 3 shows the characteristic volatile compounds of hake and tuna.

Fig. 3: Evolution of volatile compounds—alcohols, aldehydes, ketones and other compounds of hake (a–d) and tuna (e–h). The results are the mean of two determinations  $\pm$  the standard deviation. The comparison was performed using a t-test. Different lowercase letters indicate a statistically significant difference in the same sample during storage; different capital letters indicate a statistically significant difference between the two treatments at the same time. \*\* At T0, there is no capital letter because the samples are the same; therefore, no t-test was performed. T0 = 0 days; T1 = 20 days; T2 = 40 days; T3 = 60 days. Adapted from the original.

The volatile compounds in hake – mainly represented by aldehydes, alcohols and ketones – exhibited significant increases towards the end of the trial, and there was a significant difference between the glazed and control samples. In the tuna, there was an increase in these substances over the course of the storage but there were no major differences between the glazed and control samples.

We observed a difference between the control and glazed sample in hake, which was smaller than that observed in tuna, probably as a result of the 20 percent glazing. The increase in volatile compounds mirrors what was reported in the peroxide number analysis, as they are secondary and primary products of oxidation, respectively, which is also in agreement with reports from other authors.

## Perspectives

To the best of our knowledge, this is the first study focusing on the impact of different factors, such as light and oxygen, on frozen and glazed fish products over time, evaluating important safety and quality parameters during a real-time shelf-life study.

The different compositions of the two fish significantly influence their alteration. In the hake, the reapplication of the glaze played a key role in maintaining quality and led to better preservation, which was not demonstrated in the tuna (probably due to the 20 percent initial glazing). Therefore, it could be assumed that the glazing could be reapplied during bulk sales depending on the type of fish, as it is a low-cost and time-saving practice. Moreover, it should be mentioned that these products normally never stay on sale for 60 days but have a shorter shelf life. This study has shown how re-glazing can have a positive effect on fish preservation, but looking to the future, one could also consider adding functional molecules with antimicrobial and antioxidant activity to the water used for re-glazing.

## Authors

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ILENIA DOTTORI

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy



**STEFANIA URBANI**

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy



**LUIGI DAIDONE**

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy



**ARIANNA BONUCCI**

Corresponding author

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy

[arianna.bonucci@unibo.it](mailto:arianna.bonucci@unibo.it) (<mailto:arianna.bonucci@unibo.it>).



**MATTEO BECCERICA**

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy



**ROBERTO SELVAGGINI**

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy



**BEATRICE SORDINI**

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy



**RAFFAELLA BRANCIARI**

Department of Veterinary Medicine, University of Perugia, 06126 Perugia, Italy



**GIANLUCA VENEZIANI**

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy



**DAVIDE NUCCIARELLI**

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy



**AGNESE TATICCHI**

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy



**MAURIZIO SERVILI**

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy



**SONIA ESPOSTO**

Department of Agriculture, Food and Environmental Sciences, University of Perugia, 06126 Perugia, Italy

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