

## Changes of pH and peroxide value in carp (*Cyprinus carpio*) cuts packaged in modified atmosphere

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**Abstract.** The aim of our research was to examine the influence of packaging in modified atmosphere on the pH and peroxide value in muscle of common carp (*Cyprinus carpio*), as well as to determine the most suitable gas mixtures for packing of that freshwater species. Three sample groups of carp cuts were investigated. One group of carp cuts was placed on top of flaked ice placed in polystyrene boxes. Two other groups were packaged in modified atmosphere with different gas ratios: 80%O<sub>2</sub>+20%CO<sub>2</sub> (MAP 1) and 90%CO<sub>2</sub>+10%N<sub>2</sub> (MAP 2). All carp cuts were stored in the same conditions at 3±0.5°C, and on 1, 3, 5, 7, 9, 11, 13, 15, and 17 days of storage, chemical testing was performed. The results obtained indicate that the packaging of common carp under 90%CO<sub>2</sub>+10%N<sub>2</sub> slowed proteolytic reaction as well as secondary lipid oxidation.

### 1. Introduction

The quality of fresh fish is a major concern to industry and consumers. This is a complex concept involving a whole range of factors, which include safety, nutritional quality, availability, convenience and integrity, freshness, eating quality and the obvious physical attributes of the species, size and product type [1].

Fish are highly perishable and prone to vast variations in quality due to differences in species, environmental habitats, feeding habits and action of autolysis enzymes as well as hydrolytic enzymes of microorganisms on the fish muscle [2]. The high water and free amino acid content, and the lower content of connective tissue as compared to other flesh foods lead to the more rapid spoilage of fish. In general, fish have a limited shelf-life in comparison with meat products (veal, lamb, pork, poultry) as a result of the high post mortem pH in the flesh (usually > 6.0), the presence of large amounts of non-protein nitrogen (NPN), the high content of polyunsaturated fatty acids (PUFA), the presence of autolytic enzymes etc.

Deterioration of fish mainly occurs as a result of bacteriological activity leading to loss of quality and subsequent spoilage [3,4]. Microorganisms present on the surface of fish produce a large variety of hydrolytic enzymes, in particular proteases. Endogenous proteases also play an important role in the post mortem degradation of fish muscle protein [5]. These processes lead to a change to the textural and sensory characteristics of fish muscle.

Hydrolytic changes in lipids are the cause of the release of free fatty acids (FFA), which are much more susceptible to oxidative changes. Fish oil contains large amounts of polyunsaturated fatty acids which lead to the initiation of oxidation reactions and the formation of hydroperoxides of fatty acids



and other, often toxic, secondary oxidation products. The formation of peroxides (measured by the peroxide value; PV) is considered an indicator of the rate of primary oxidation, while the thiobarbituric acid (TBA) value is an indicator of secondary oxidation [6,7].

The changes in lipids of fish are responsible for the quality deterioration with the extended storage, especially under inappropriate conditions. They involve lipolysis, lipid oxidation, and the interaction of the products of these processes with nonlipid components such as protein. Fish muscles contain an abundance of long chain lipids with a high proportion of polyunsaturated fatty acid that undergoes changes due to oxidation during processing and storage.

The shelf-life of fresh chilled fish is relatively short and at ambient temperatures of  $2\pm 2^{\circ}\text{C}$  it is about 2 to 3 days. The shelf life of fresh chilled fish can be extended by vacuum packaging or modified atmosphere packaging (MAP) [8,9].

The aim of this research was to monitor changes of selected chemical parameters of common carp (*Cyprinus carpio*) steaks packaged in modified atmosphere during the storage at  $3\pm 0.5^{\circ}\text{C}$  and to determine the shelf life of the products.

## 2. Materials and Methods

### 2.1. Sample collection

Samples from fourteen common carp (*Cyprinus carpio*) of average body weight of  $2.50\pm 0.30$  kg were obtained from fishpond where a semi-intensive rearing system was used. Fish were transported live to the fish slaughtering and processing facility, where they were stunned, slaughtered, scaled, and carcasses were cut into steaks 2 cm thick and 220 g average weight. The carp steaks were divided into three groups.

The control fish steak group was placed on top of flaked ice placed in polystyrene boxes with outlets for water drainage. The ice/fish ratio was 3:1 and maintained constant throughout the experiment. The other two sample groups of carp steaks were packaged in modified atmosphere with different gas ratios: MAP1:80% $\text{O}_2$ +20% $\text{CO}_2$  and MAP2: 90% $\text{CO}_2$ +10% $\text{N}_2$ . The machine used for packaging the carp steaks was Variovac (Variovac Primus, Zarrentin, Germany), and material used for packaging was foil OPA/EVOH/PE (oriented polyamide/ethylene vinyl alcohol/polyethylene, Dynopack, Polimoon, Kristiansand, Norway) with low gas permeability (degree of permeability for  $\text{O}_2$  – 3.2  $\text{cm}^3/\text{m}^2/\text{day}$  at  $23^{\circ}\text{C}$ , for  $\text{N}_2$  – 1  $\text{cm}^3/\text{m}^2/\text{day}$  at  $23^{\circ}\text{C}$ , for  $\text{CO}_2$  – 14  $\text{cm}^3/\text{m}^2/\text{day}$  at  $23^{\circ}\text{C}$  and for steam 15  $\text{g}/\text{m}^2/\text{day}$  at  $38^{\circ}\text{C}$ ). The ratio of gas:carp steak in the packages was 2:1. All samples were stored in the same conditions at  $3\pm 0.5^{\circ}\text{C}$  and on 1, 3, 5, 7, 9, 11, 13, 15 and 17 days of storage, chemical testing was performed.

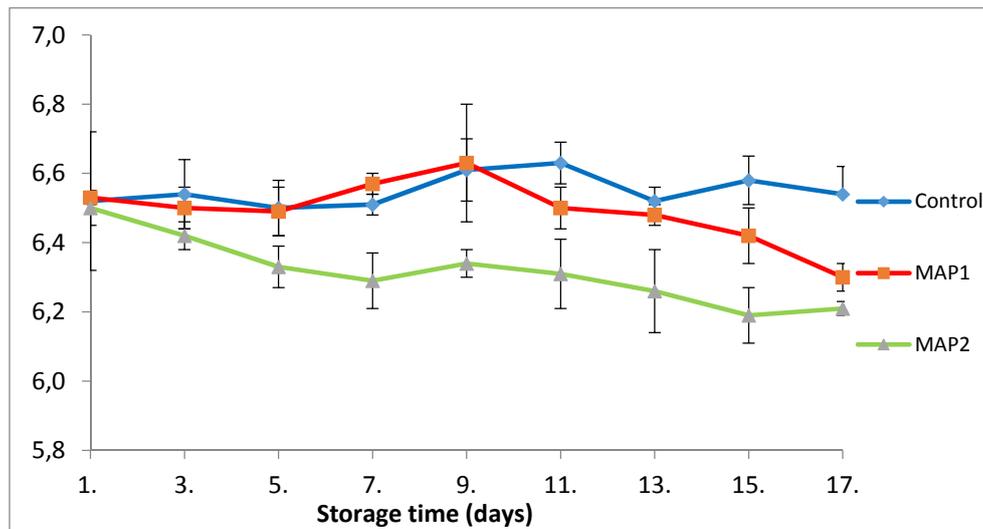
### 2.2. Chemical analysis

Muscle pH was measured by Cyber Scan pH-510 digital pH-meter (EUTECH Instruments, Netherland). PV, expressed in milliequivalents of peroxide oxygen per kilogram of fat, was determined by EN ISO 3960:2009 method.

### 2.3. Statistical analysis

The mean values and standard deviations were calculated by using column statistics for the six values in each analysed group. Significant differences between groups were calculated by using one-way ANOVA analysis by Tukey's comparative test in the program Microsoft Office Excel (2010). Differences were considered as significant when p value was  $< 0.05$ .

## 3. Results and Discussion



**Figure 1.** Changes in pH value of common carp steaks packaged under different conditions during the storage period.

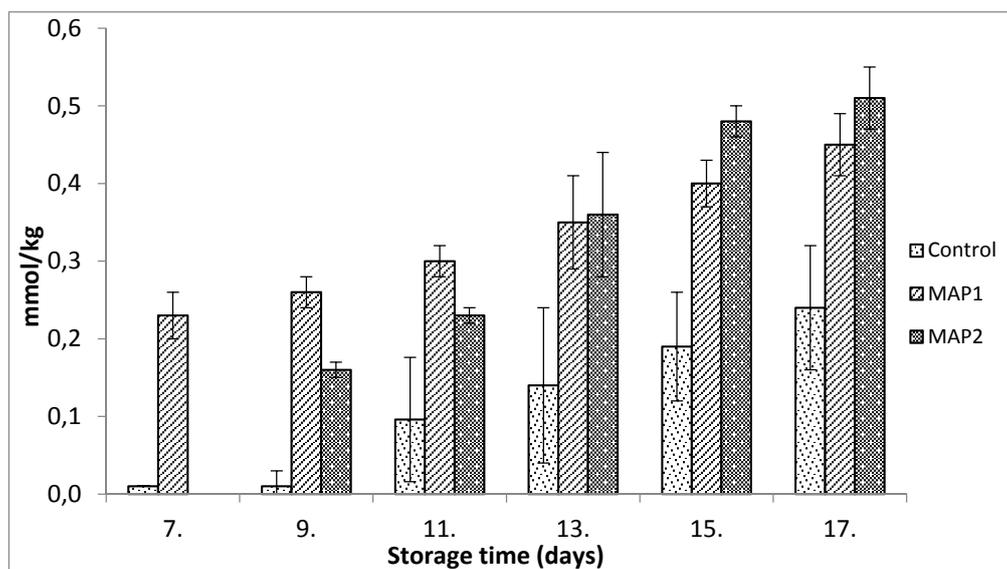
Figure 1 shows pH values in common carp steaks depending on the type of packaging and the length of the storage period. In MAP1 carp steaks, significant ( $p < 0.01$ ) a pH increase was observed between day 5 (pH:  $6.49 \pm 0.03$ ) and day 9 (pH:  $6.63 \pm 0.06$ ) of the experiment. From then on, the pH value began to decrease and reached  $6.30 \pm 0.04$  on storage day 17. In contrast, a decrease in pH value was detected in carp steaks in MAP2 during the whole experimental period. The lowest pH value of  $6.19 \pm 0.02$  in this experimental group was recorded on storage day 15. pH values of control carp steaks fluctuated during the storage period, and ranged from  $6.51 \pm 0.09$  to  $6.63 \pm 0.03$ . Compared to control carp steaks, MAP packaged fish in the  $90\%CO_2 + 10\%N_2$  atmosphere had a lower pH during the entire storage period, while the pH in carp steaks packaged in MAP1 was significantly lower ( $p < 0.01$ ) after 9 days of storage. The mean pH value for the control fish and carp steaks packaged in MAP1 and MAP2 throughout the storage period was  $6.55 \pm 0.08$ ;  $6.49 \pm 0.06$  and  $6.32 \pm 0.07$ , respectively.

The pH values in the muscle tissue of live fish are close to 7.0, but the post mortem pH generally ranges from 6.0 to 7.1, depending on the season of the year, fish species and other factors. Due to the amount of lactic acid produced during glycolysis under anaerobic conditions, the post mortem pH of fish muscle decreased, while the degree of pH reduction influenced quality of fish meat [10].

As shown in figure 1, the lowest pH value was recorded in carp steaks packaged in  $90\%CO_2 + 10\%N_2$ . Other authors [4,11,12] also recorded significantly lower pH values in fish samples packaged in modified atmosphere with higher percentage of  $CO_2$ ; this is explained by dissolution of  $CO_2$  in the fish muscle, which is associated with increase of carbonic acid production.

The moderate increase of the pH in MAP1 carp steaks after five days of storage can be attributed to the higher quantity of basic compounds produced by the activity of fish spoilage bacteria [13], which had favourable growth conditions because of high concentration of  $O_2$  in this gas mixture.

The pH values of common carp muscle in our research as well as differences in pH values under various experimental conditions during storage correspond to the findings of other authors [8,14,15].



**Figure 2.** Changes in PV of common carp steaks packaged under different conditions during the storage period

Figure 2 shows the PV in the carp steaks depending on the type of packaging and the length of the storage period. In our research, during the first five days of storage, peroxide was not detected in both unpackaged and packaged fish meat. Later during the study, the PV was lower in control carp steaks than in those packaged in MAP. From day 7 to day 13, PV values were at highest level in carp steaks kept in the oxygen-rich atmosphere (80%). At the end of the study (day 15 and day 17), PV values were higher in fish packaged in the atmosphere without oxygen. As reported by Jayasingh *et al.* [16], lipid oxidation was higher in carp steaks packaged in MAP with 80% O<sub>2</sub> than in control fish, exposed to ambient air, which is in agreement with the results of the present study. As concluded in Ruiz-Capillas and Moral [13], lipid oxidation depends on the synergy effect between CO<sub>2</sub> and O<sub>2</sub>. For that reason, lipid oxidation in an atmosphere with 40% O<sub>2</sub> could be more intensive compared with atmosphere with 60% O<sub>2</sub>. Fluctuations in PVs that have been recorded in our research are in line with the results of other authors [6], pointing out the fact that PV cannot be considered as suitable indicator of fish muscle freshness.

#### 4. Conclusion

Packaging common carp under 90%CO<sub>2</sub>+10%N<sub>2</sub> slowed proteolytic reaction as well as secondary lipid oxidation. According to those indicators, packaging common carp in 90%CO<sub>2</sub>+10%N<sub>2</sub> is more suitable compared to packaging in an 80%O<sub>2</sub>+20%CO<sub>2</sub> gas mixture.

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