日本冷凍空調学会論文集
Trans. of the JSRAE
Vol.23, No. 1 (2006)
pp.79～84
原稿受付:平成17年10月4日

論　文

Application of the Oxidation-Reduction Potential (ORP) for Pre-grading Tuna Freshness On-board

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SUMMARY

Application of ORP as a rapid indicator for grading tuna's freshness on the ship was studied. The long line trawling process was used for catching the sample tuna in the South Pacific Ocean. All captured sample tuna were weighed, gender identified and investigated for their mortality, then measured ORP and K value. Three species of tuna were caught: blue marlin (*Makaira mazara*), yellow fin tuna (*Thunnus albacares*), and swordfish (*Xiphia* gladius). Most of the fish captured were male and they had been dead after picking onboard. The measured ORP values of blue marlin varied in the range of 0.295-0.362 Volt, with pH between 5.35-5.84. Both ORP and pH of swordfish was similar to that of blue marlin. But for yellow fin tuna, the ORP value was about the same as blue marlin while its pH was significantly higher. ORP value in all species tended to increase with pH of the fish meat decrease. It is interesting that ORP value of tuna increased in correlation with K value. These results suggested that ORP and pH change, which are measured in the short time, are the effective indicators for grading tuna's freshness on-board.

Key words: ORP, pH, tuna, grading method, long line trawling, freshness, K value

1. INTRODUCTION

There is a great demand for the high quality tuna meat in Japanese market. For instance, in Tokyo fish market alone, over 250 tons of tuna are sold by auction in each week[1]. Despite of such importance, only few studies on the changes of freshness of tuna species comparing to those of other fish have been reported. The reason was mainly due to the difficulty of getting samples with known history of catching. This also resulted in uncertain price judgment due to the changes in market trend. Although freshness is considered as the most important factor in grading the quality of tuna meat, exporters or buyers often decide the price of the tuna meat without considering the scientific information. Methods for grading tuna also vary in each locality, however, at present, two kinds of traditional and sensory grading methods using tail meat were used[2] in the auction. In the first method, a piece of tail meat would be cut before auction. The conditions of meat color, oil and water consistency were inferred with the observation on the surface of tuna meat. In the second method, a cylindrical tuna meat sample would be cut out by a borer to examine on the whole meat and the color of the blood vessel. The blood vessel for fresh tuna should be pink or red; brown is not good. Nowadays in the market, the freshness assessment is generally carried out by experience through observing meat color, blood vessel, and muscle firmness. Recently, since the new trading system or the bulk buying of the whole shipment has been increased, pre-grading system or a rapid method for evaluating tuna's quality on the fishing ship has been required.

However, due to lacking of experts for grading, and having limited time to evaluate each sample independently, therefore, a non-destructive, simple yet reliable method for assessing tuna's quality is required today. We have found that it is possible to estimate the changes of freshness the initial stage after catching by measuring oxidation-reduction potential (ORP) and pH changes. In the present study, the application of ORP to evaluate fresh tuna samples is carried out on the tuna ship, which was operated in the South Pacific Ocean.

2. MATERIALS AND METHODS

A large-scale longline ship from Tokyo University of Marine Science and Technology, namely Shinyomaru, departed from a port in Tokyo headed to the East Caroline Basin above Indonesia (at 149°14.046 E and 2°29.938 N). Longline trawling process was used as the method for catching oceanic fish. The total length of the trawl was approximately 40 kilometers. Five hooks were connected between two successive floats. Altogether the total number of hooks was 750 per one operation. In each day, the longline gear would be placed in the ocean for about 8 hours before being taken back to the ship. During this process, if a tuna was caught, it will be investigated as follow.

Tuna after being caught and arrive on the ship

↓

Weigh, identify species, mortality and gender

↓

Separate the tail part from the body by a knife

↓

Slice the muscle and remove the skin

↓

Measure the ORP and pH at 0.5 cm. depth from the surface

↓

Take and weight 1 g of the muscle

↓

Store the muscle in 5% Perchloric acid vial

↓

Kept in frozen state at –60°C

↓

Analyze of K-value by modified Ryder method[3]

It should be noted that these steps of sample preparation in the above diagram were carried out at 25°C and the fish were handled immediately after arriving onboard and finished within 1 hour before conducting ORP/pH measurement. Measurement of ORP and pH was carried out by a direct contact method between the electrode probes and tuna sample. A commercially available ORP/pH meter (Toko^{TM} TPX-90I, Toko Chemical Laboratory Co., Tokyo) consisting of a platinum (PCM 308S-SR) and a glass electrode (PCE308S-SR) has been used for measurement of ORP and pH change respectively. Both electrodes are specially designed for capable of measuring ORP and pH in liquid and solid states. The quinhydron standard solution, which has ORP of 0.26±0.02 Volt, was used for electrode calibration between each reading.

ORP Measurement

The oxidation-reduction potential is defined as the measurement of electrode potential to estimate the degree of oxidation or reduction of a particular foodstuff. The redox potential (E_h or ORP) of a reversible redox reaction is given by the equation derived by Nernst.[4] It is expressed as follow:

$$E_h = E_o + \frac{RT}{nF} \ln \frac{[oxidant]}{[reductant]}$$

in which E_o is the standard redox potential at pH 0, but with other solute components present at 1 M concentration (its value is assumed to be equal to the theoretical value for redox couple in dilute aqueous solutions); R is the molar gas constant; T is the temperature in K; F is the Faraday quantity of electricity; n is the number of electrons transferred in the reaction; and ln is the natural logarithm.

In general, an ORP range of pure water in relation to its pH is expressed by the following equations (1) and (2)[5,6] based on the Nernst equation:

$$ORP = 1.23 - 0.059pH \quad (O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O) \qquad (1)$$

$$ORP = -0.059pH \quad (2H^+ + 2e^- \rightleftarrows H_2) \qquad (2)$$

Equations (1) and (2) represent boundaries of oxidizing and reducing decompositions of water, respectively, which correspond to the upper and lower solid lines indicated in Figure 1. Hence, under ambient environment, water exists in a region enclosed by these upper and lower boundary lines.

According to the study conducted by Okuochi et.al[7], in order to define the equilibrium ORP value of water, pure water samples (deionized and ultrafiltered water) were equilibrated through sufficient exposure to air at a constant temperature. And then measured equilibrium ORP values of these samples while varying their pH values with NaOH or KOH as an alkali reagent and HNO_3 or HCl as an acid reagent. Thus, an equilibrium ORP-pH relationship of pure water was experimentally elucidated as expressed by the following equation

$$ORP = 0.84 - 0.047pH \qquad (3)$$

Equation (3) corresponds to the broken line indicated in Figure 1. ORP values on this broken line indicates a state of the equilibrium ORP level of water. ORP values above this broken line belong to the oxidation region of water, and ORP value below it belong to the reduction region of water. Under the condition that there is no influence by external energy, microbial decomposition, or any other action, an ORP value in the oxidation or reduction region will eventually shift to the equilibrium ORP level with the lapse of time.

3. RESULTS AND DISCUSSION

Table 1 Classification, gender, and weight of tuna captured during Feb. 5-12, 2005

Sample No.	Body temp (°C)	Species	Mortality	Sex	Weight (kg)
1	26.0	Blue marlin	dead	♂	60
2	26.6	Blue marlin	dead	♂	63
3	26.1	Blue marlin	dead	♂	79
4	26.5	Blue marlin	dead	♀	37
5	26.0	Blue marlin	dead	♂	64
6	26.6	Yellowfin	dead	♂	10
7	26.2	Blue marlin	dead	♂	53
8	26.5	Blue marlin	dead	♂	66
9	26.7	Blue marlin	dead	♂	37
10	28.7	Swordfish	dead	♀	37
11	26.5	Blue marlin	dead	♂	44

From table 1, it was found that there were 3 species of tuna caught altogether: blue marlin (9 samples), yellowfin tuna (1 sample) and swordfish (1 sample). Most of the fish were male and the average temperatures of their bodies were about 26-28°C. All samples had been dead after picking up on-board. These samples were used for subsequent ORP and pH measurement.

Japan and the United States are two main importers of sashimi grade tuna. The grading of tuna quality is similar in both countries, but there are some differences as well. In Japan the order of ranking are A (top quality), B, C and D (reject) with the overall evaluation. In west coast US markets, fish are ranked or graded #1 (top quality), #2, #3, or #4 (reject), with a plus or minus sign to indicate the presence or absence of fatty layer. Thus the highest grade is #1+. Basically only larger fish can be #1 grade (must be approx. 30 kg whole weight for yellow fin tuna or 40 kg whole weight for other species)[8]. However, these criteria can be varied with market demands. Therefore, most of tunas captured in this study were in large size (weigh more than 40 kg), except samples number 4,6,9,10, which was considered to be medium size.

Table 2 ORP and pH of blue marlin, yellowfin tuna and swordfish caught by long line trawling process

Sample	ORP (Volt)	pH	K value (%)
Blue marlin	0.362 ± 0.012^{c}	5.35 ± 0.05^{a}	15.35 ± 0.24^{f}
Blue marlin	0.334 ± 0.009^{b}	5.54 ± 0.03^{b}	12.62 ± 0.23
Blue marlin	0.323 ± 0.06^{b}	5.50 ± 0.03^{b}	12.35 ± 0.39^{b}
Blue marlin	0.320 ± 0.004^{b}	5.45 ± 0.05^{ab}	14.54 ± 0.30^{e}
Blue marlin	0.295 ± 0.009^{a}	5.66 ± 0.04^{c}	9.32 ± 0.18^{a}
Yellowfin	0.332 ± 0.013^{b}	5.80 ± 0.08^{d}	11.19 ± 0.14^{b}
Blue marlin	0.333 ± 0.005^{b}	5.51 ± 0.09^{ab}	12.85 ± 0.13^{c}
Blue marlin	0.306 ± 0.003^{a}	5.84 ± 0.02^{d}	8.92 ± 0.27^{a}
Blue marlin	0.305 ± 0.007^{a}	5.61 ± 0.02^{c}	9.81 ± 0.17^{a}
Swordfish	0.327 ± 0.006^{b}	5.46 ± 0.04^{a}	13.68 ± 0.35^{de}
Blue marlin	0.333 ± 0.006^{b}	5.55 ± 0.03^{bc}	11.78 ± 0.22^{b}

Data that have same superscripts are not significantly different at 95% confidence level ($p>0.05$)

From Table 2, the ORP values of blue marlin (*Makaira mazara*) vary within 0.295-0.362 Volt. with pH between 5.35-5.84. Obviously, these results suggest that the initial values of ORP and pH of blue marlin samples varied significantly although all samples were caught by the same fishing method. These differences are probably due to the time span from hooking to death, although we could not know the actual time span. For yellowfin tuna (*Thunnus albacares*), though ORP values were almost the same as blue marlin but its pH is significantly higher. In contrast, both ORP and pH of swordfish (*Xiphia* gladius) were similar to that of blue marlin. Overall, the ORP values in this study are in fairly good accordance with the previous results obtained from Agustini et. al., which reported the changes in ORP of yellowfin tuna in the range between 0.31-0.37 Volts during refrigerated storage[9].

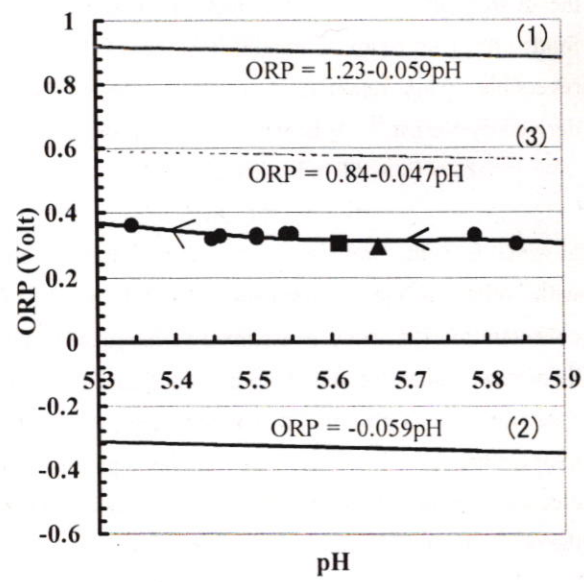

Fig. 1 Relationships of ORP and pH in the tail muscle of blue marlin (*Makaira Mazar*; ●), yellowfin tuna (*Thunnus albacares*; ▲) and swordfish (*Xiphia gladius*; ■).

The relationship between ORP and pH of these three species of tuna is illustrated in Figure 1. Upper and lower solid lines (1) and (2) represent theoretical boundaries of oxidizing and reducing decompositions of pure water, respectively. Under ambient environment, water will usually exist in a region enclosed by these upper and lower boundary lines. However, ORP values on the broken line (3) indicate a state of the equilibrium ORP level of pure water. ORP values above this broken line belong to the oxidation region of water, and ORP value below it belong to the reduction region of water.

Interestingly, it was found that ORP values of all tuna samples were in the reduction region below the equilibrium ORP level. Moreover, it can be observed that these ORP values tend to increase when the pH values of fish meat decrease (shift towards the arrows' direction). Theoretically, under the condition that there is no influence from microbial deterioration, an ORP value in this reduction region will eventually approach to the equilibrium ORP level with the lapse of time. The pH values of these three species were in the vicinity of weak acidity (pH 5.35-5.84). In fact, when the fish was subject to physical stress or struggling during catching, lactic acid will be produced and accumulated in the muscle, which causes the pH of the meat to drop. The lactic acid content in the muscle usually promote the loss of freshness during storage[10]. This drop in pH was in agreement with K values change. As we can observe from table 2, blue marlin samples, which had lower initial pH, would have relatively higher K values. This suggests that although the fish were captured in the same batch but they might have different freshness qualities. And such differences could not be easily distinguished by just observing meat color or the blood vessel alone. However, K values of all samples were still in the range under 20%, which indicate that they were considered fresh and suitable to be consumed as Sashimi[11].

The correlation between ORP and K values are shown in Fig. 2, and the simply calculated correlation coefficient of two parameters is 0.791. The initial ORP values show the distributions in two groups as shown in Fig. 2. In the group 1, ORP values are under 0.306, and K values are under 10%. In the group 2, ORP values are higher than that of group 1, and K values are over 11%. Regarding to the report of Augustini et.al[12], that investigated changes in K value of blue fin tuna, it was observed that the ORP increased along with K value until reaching a maximum value then decreased rapidly after bacterial spoilage took place. Although this study do not aim to investigate ORP changes during storage, however the ORP values measured in the present study, which already had high initial K value even after captured, would likely reach the maximum ORP value sooner than those samples with lower initial K values.

Following the judgments of K value, ORP and pH changes, all tuna captured in this trip can be graded into 2 groups. Group 1, which have very good freshness quality (K value 8.92-9.32%, ORP between 0.295-0.306, pH 5.61-5.84) include sample no. 5, 8, 9. The rest of the samples should be graded into group 2, which have lower freshness but still be able to consume as Sashimi (K value 11.19-15.35%, ORP between 0.32-0.362 and pH 5.35-5.55) respectively. These results suggested that ORP value is the effective indicator for grading tuna's freshness on-board. However, for the certain corroboration of the relationship between the freshness of tuna and ORP values, further many data measured on-board are required.

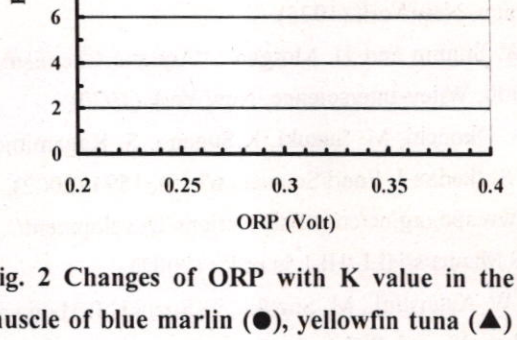

Fig. 2 Changes of ORP with K value in the tail muscle of blue marlin (●), yellowfin tuna (▲) and swordfish (■).

4. CONCLUSION

Though assessment of tuna freshness on-board seems to be difficult in practice due to requirement of an expert. However, there is a possibility to evaluate fish freshness from very initial stage by monitoring ORP changes. Measurement of ORP gave reliable results between each repetitive reading and it was sensitive enough to be able to differentiate the freshness of newly caught fish. Furthermore, due to its simplicity in measurement, ORP is useful as a rapid freshness index for pre-grading of tuna on-board before the fish were actually graded and auctioned in fish market.

ACKNOWLEDGEMENT

The author would like to thank, all officers and crews on the Shinyomaru ship for their kind support in this research.

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