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Short Paper

The possibility of using oxidation–reduction potential to evaluate fish freshness

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K value is a fish freshness index available for evaluating the initial stage of fish deterioration and it has been used widely for judging fish that is to be eaten as sashimi (raw meat fish in Japan). This index is based on nucleotide degradation, which is expressed as a percentage of the amount of inosine and hypoxanthine to the total amount of adenosine 5′-triphosphate (ATP) and its related compounds.[1,2] However, *K* value fluctuates significantly depending on the species being tested and the procedures for measurement are usually tedious and time consuming.[3]

Generally, upon assessing food material as an ecological environment for pathogenic microorganisms, factors such as pH, water activity, and presence of salt or other preservative agents are considered.[4] However, little attention has been paid to the food's oxidation–reduction potential (ORP), although its measurement procedure is as simple as that for determining pH.

A report by Huss and Larsen dealt with the correlation between the state of deterioration and the ORP changes of different fish.[4] Their results showed that the ORP of fish increased initially and subsequently decreased. However, since their study was concerned mainly with the later stages of deterioration, the results not only have limited data about the initial stages, but also give no explanation for the initial increase in ORP. In addition, we could not find any study on the relationship between ORP and *K* value.

Recently, it has been known that fatigue in humans can be evaluated by measuring the ORP changes in urine (S Okouchi, pers. comm., 2000). This fact suggests that the ORP is sensitive to metabolic changes, which may correlate with the *K* value in the case of fish. The present study was carried out to examine the possibility of using the ORP as a means of characterizing fish freshness, especially by focusing on the initial stages of fish deterioration.

Fresh samples of yellowfin tuna *Thunnus albacares* purchased as fillet from retail shops were cut in cubes (3 cm × 2 cm × 1.5 cm) and wrapped in polyethylene bags before being stored at 10°C, 5°C and 0°C for 7 days. The ORP measurements were carried out using an electrometer as described by Okouchi *et al.*,[5] in which platinum and glass electrodes were used to measure ORP and pH, respectively. Because the electrode was especially designed for measuring the ORP of human body surfaces, the ORP of the sample was measured by putting the electrode directly on the surface of the samples. Before use, the electrode was checked with quinhydron standard solution, which has an ORP of 0.26 ± 0.02 V. Between repetitive readings, the electrodes were cleaned and soaked in distilled water for several minutes before the next measurement. The *K* value was measured by using high pressure liquid chromatography (HPLC) based on the modified method of Ryder.[6] Analyses of the samples were carried out in triplicate.

Figure 1 shows the changes in the ORP and pH values during storage. The ORP of the samples increased initially at all storage temperatures.

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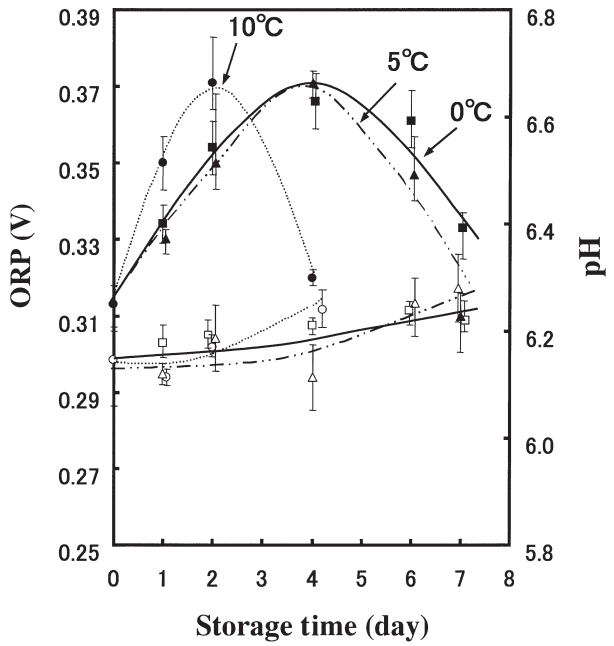

Fig. 1 The change of the oxidation–reduction potential and pH values of yellowfin tuna *Thunnus albacares* during storage at different temperatures. Oxidation–reduction potential: (●) 10°C; (▲) 5°C; (■) 0°C. pH: (○) 10°C; (△) 5°C; (□) 0°C. Each symbol is represented as the mean ± SE. To show the clarity of SE data, the symbol is slightly shifted.

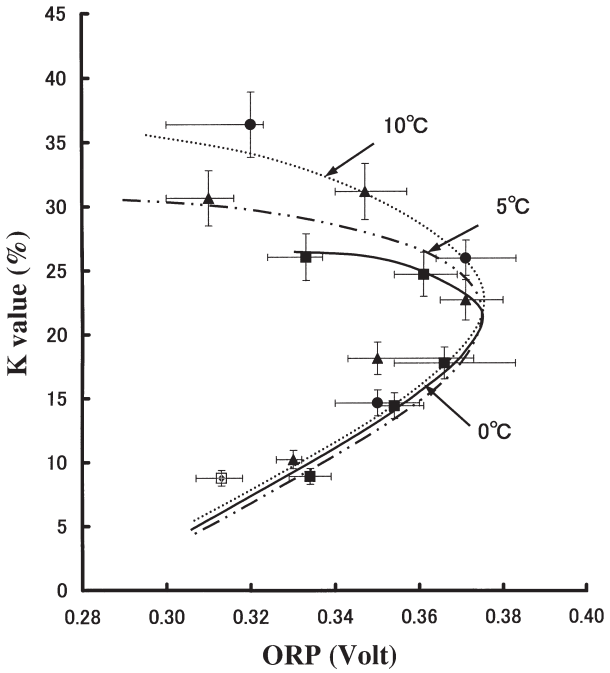

Fig. 2 The relationship between the K and oxidation–reduction potential values of yellowfin tuna *Thunnus albacares* during storage at (●) 10°C; (▲) 5°C; (■) 0°C. Each symbol is represented as the mean ± SE.

Once the ORP reached approximately 0.37 V after a certain period of time, it started to decrease, whereas pH did not change significantly. The reason as to why there was a small change in pH is because the sample used in the present study was in the stage following the sudden drop in pH after death. However, changes in the ORP was noticeable during this stage. These results clearly suggest that ORP is more sensitive than pH for evaluating the change in fish freshness after the pH has dropped.

The time required for the ORP to reach the maximum value of 0.37 V appears to be dependent on the storage temperature, although the difference between 0°C and 5°C was not significant.

Figure 2 shows the relation between ORP and *K* value, in which the ORP increased proportionally to the *K* value and started to decrease when the *K* value reached 20–25%. Interestingly, it has been demonstrated that when the *K* value results in the maximum ORP, this is in indication of limited freshness for eating raw fish (sashimi in Japan).[3] The results of the present study also show that at the initial stages of deterioration, the relationship between the ORP and *K* value is almost independent of storage temperature and has a fairly positive correlation. Whereas, at the later stages of deterioration, in which the *K* value is above 20–25%, the ORP decreased with increasing *K* value depending on storage temperature. This means that the ORP might be affected by other factors other than the *K* value.

When considering the application of ORP for evaluating fish freshness, it should be noted that a fish sample with a given ORP would have two *K* values owing to the parabolic form of the *K* value–ORP curve. This fact makes it difficult to use ORP as a single index for characterizing fish freshness. Therefore, for the time being, it cannot be concluded whether ORP is useful for evaluating fish freshness. However, we believe that the use of ORP might be potentially useful for assessing fish freshness, especially at the initial stages of fish deterioration because a remarkable correlation between ORP and *K* value was confirmed. In addition, the mechanism underlying the changes in ORP, particularly at the initial stages of fish deterioration, still needs further clarification. Regarding this situation, the differences in the ORP changes during storage among different fish species is currently being investigated and it can be confirmed that yellowtail, red seabream and Japanese flounder showed the same trend (TW Agustini *et al.*, unpubl. data, 2001). The results of this latter study are yet to be published.

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