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［課程博士］

博士学位論文内容要旨

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論文題目 Factors affecting the oxidation-reduction potential (ORP) change during initial deterioration of freshness in fish and shellfish

This study investigated factors affecting ORP change during initial deterioration of freshness in fish and shellfish. The results in chapter 2 suggest the mechanism underlying the change of ORP at the initial stage is due to two major reasons.

Firstly is the effect of postmortem decrease in pH of the muscle. Most pH in fish and shellfish muscle usually drops after death due to the glycolysis and lactic acid accumulation. Therefore, regardless of other factors involve, the ORP will increase as the pH of the muscle decrease. Secondly, the ORP generally increases during the initial autolytic phase due to enzymatic degradation of ATP in fish and shellfish muscle. The oxidation of hypoxanthine to uric acid by activity of xanthine oxidase is the key reaction in the pathway that affects ORP increase.

However, at the later stage of freshness deterioration, one of the major spoilage reactions is the bacteriological reduction of trimethylamine oxide (TMAO) to trimethylamine (TMA).When TMAO is reduced to TMA the redox potential will decrease and the pH increases. However, there was no direct correlation between ORP and changes in TMAO or TMA content during storage. The growth of H_2S producing bacteria, which can reduce TMAO to TMA, is also responsible for the decrease in ORP at the later stage of deterioration.

The increase of ORP values in the fish muscle at early days of storage is unlikely owing to the effect of lipid oxidation since the oil was stable and did not undergo oxidation during storage at 5 ^{o}C. However, as the autooxidation of lipid progresses slowly, the ORP tends to increase upon the storage time due to the presence of hydroperoxides and secondary oxidative products.

Myoglobin, a complex of globin and heme, is the major pigment in some red flesh fish. Myoglobin can undergo autooxidation and result in undesirable brownish color of the tuna meat. In chapter 3, discoloration in meat color of yellowfin tuna (*Thunnus albacares*) and its relationship with oxidation-reduction potential (ORP) changes was studied. During storage at 5^{o}C, yellowfin tuna meat undergoes discoloration as a result from the oxidation of ferrous myoglobin derivatives (Mb and OxyMb) to ferric metmyoglobin. This autooxidation of myoglobin yields an electrical potential, which can be measured by an ORP meter. It was found that the ORP change of myoglobin extract and the development of metmyoglobin (MetMb) were significantly correlated. The ORP increased significantly as the metmyoglobin increased from 9.175% to 27.898% and stabilized when metmyoglobin content reached 60.97%. A plot between ORP values against ln [Mb]/[MetMb] yields a linear equation. The interception of this line shows an apparent, $E_{0\,(app)}$, which the apparent standard potential of myoglobin/metmyoglobin system at a dilute concentration, equals to 0.201 V. Moreover, the changes in K value were significantly correlated with changes in metmyoglobin content. Tuna meat, which is acceptable for sashimi (K value below 20%), should have metmyoglobin content less than 40% and redness (a-value) higher than 3.5.

In Chapter 4, effects of rearing conditions on ORP change and ATP degradation of live and dead scallops (*Pecten yessonensis*) were investigated. Scallops were divided into three groups and subjected to three different rearing conditions: rearing at higher-than-optimum temperatures (at 15-18°C) with aeration, rearing in seawater but without aeration, or removal from seawater and live storage in air at 10°C. The ORP and pH of the adductor muscle of live scallops during rearing were measured at regular time intervals for 24 h. then the adductor muscle in each sample was removed from the valves and stored at 0°C. Changes in ORP, K value, ATP degradation, and D-lactic acid content in the adductor muscle were monitored. The results showed that live scallops had a reductive characteristic in term of ORP, which varied between 0.16-0.19 V. and a pH ranged from 6.2-7.0. However, during storage, ORP increased towards a more oxidative state and eventually remained constant in all rearing conditions. ORP also increased with K value and approached its maximum when K value exceeded 25%. Regardless of rearing conditions, an ORP range which indicated the reasonable freshness of scallop for sashimi was 0.166-0.215 V. Postmortem initial ATP contents were highest in the scallops reared in seawater with aeration whereas the fastest ATP degradations were observed in live storage samples. D-lactic acid accumulations in the muscle were lowest in the samples reared in seawater with aeration. It was found that the absence of oxygen supply during rearing enhanced ATP degradation and D-lactic accumulation.

In Chapter 5, application of ORP as a rapid indicator for pre-grading tuna's freshness on the ship was studied. The long line trawling process was used for catching tunas in the South Pacific Ocean. All captured samples 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 when picking up 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 close to that of blue marlin. However, for yellow fin tuna, although ORP values were about the same as blue marlin but their pH were significantly higher. ORP values in all species tend to increase as 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, can possibly be used as an indicator for pre-grading tuna's freshness on-board.

The overall results suggested that there were correlations between ORP and postmortem biochemical changes in fish and shellfish muscle at both initial and later states with different factors involved. Therefore, it is recommended that ORP be used with other sensors to assure more accuracy in assessing freshness of fish and shellfish.