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Research on quality changes and indicators of *Pandalus borealis* stored under different cooling conditions

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Abstract: The quality changes of Northern shrimp, *Pandalus borealis*, stored in ice, liquid-ice or salt-water mixed with ice, either at ambient temperature of -1.5 or 1.5 °C, were evaluated by using sensory assessment, physical methods, chemical and microbial analysis. Storage in liquid ice was more effective than ice or salt-water mixed with ice, in delaying spoilage of the shrimp. It was observed that the total volatile nitrogen (TVB-N) content decreased during the first day in shrimp stored in liquid ice at both -1.5 °C and 1.5 °C and its formation was further delayed for 3 days in shrimp stored at -1.5 °C. In other groups the TVB-N content increased with time. The trimethylamine (TMA) value increased gradually with storage time, in all samples, except for the one stored in liquid ice at -1.5 °C during the first day of storage. Total viable counts (TVC) showed that bacteria grew most quickly in shrimp stored in ice and in salt-water ice, followed by those in liquid ice at 1.5 °C or -1.5 °C respectively throughout the storage period. Lowest counts were observed in sample stored in liquid ice at -1.5 °C where the lag phase of growth of bacteria was apparently extended at the beginning of storage. Principal component analysis (PCA) and analysis of variance (ANOVA) were performed to analyse the variation and correlation of indicators. The results show good correlation between some of the quality indicators, TVB-N, TMA, TVC, pH, NH₃ response of electronic nose and sensory evaluation.

Key words: *Pandalus borealis*; liquid ice; superchilling; electronic nose; sensory evaluation; spoilage

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1 Introduction

The Northern shrimp (*Pandalus borealis*), a cold water shrimp, is primarily harvested in the areas of north sea. For example, it is estimated that 70 000 tons were landed in Newfoundland and Labrador in 2001^[1]. Various techniques and methods have been developed over the years to reduce enzyme and microbial activity in order to prolong the shelf life of shrimp. Freezing technique is common in many seafood processing companies. However, deterioration of texture and flavor is a frequent problem for frozen product. Fresh seafood products stored in ice, including fresh shrimp, have always been the consumer's primary choice. Methods that have been used to prolong shelf life of unfrozen products are: chilling in ice^[2-4], chilling in liquid ice^[5], ice storage^[6], superchilled storage at $0-4$ °C^[7,8], modified atmospheres packaging storage in ice^[9,10], gamma radiation^[11], and treatment with

organic acids and their salts^[12,13].

The assessment of quality and shelf life of seafood is based on sensory, chemical and microbiological tests. Chemical test, like analysis of trimethylamine (TMA), total volatile nitrogen (TVB-N), have been employed to evaluate spoilage of seafood^[14-16]. Trimethylamine (TMA) is formed during storage by the activity of certain species of bacteria on the substance trimethylamine oxide (TMAO). Therefore determination of TMA content is a measure of bacterial activity and spoilage^[17]. Increase in TMA during iced storage is similar to increases in bacterial numbers^[18]. The measurement of total volatile basic nitrogen (TVB-N) is often used as an alternative to measuring TMA content because the bases contain ammonia, trimethylamine, and dimethylamine. The use of TVB as an index of freshness is confined to those species where TMA can be used as an index to fish or shrimp in ice^[14,19]. An estimation of the total viable counts (TVC) is

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usually used as an acceptability index in standards, guidelines and specifications^[20]. The electronic nose, which has been developed in recent years, is a rapid evaluation technique to monitor the freshness of fish products^[21,22]. Many studies have shown that measurements using electrochemical sensors correlate well with classical methods to evaluate freshness and spoilage of seafood, that is TVB-N measurements and sensory analysis, for capelin^[21,23] herring and fresh roe^[24], and whole or peeled shrimp^[25]. Sensory evaluation is an important method for the assessment of freshness and quality, and is commonly used in the fish sector and fish inspection services^[26]. QIM schemes have currently been developed for a number of fish species including fresh herring, cod, red fish, Atlantic mackerel, mackerel, European sardine, brill, dab, haddock, pollock, sole, turbot, shrimp and Atlantic salmon^[27].

There is little information on the quality deterioration of the shrimp stored in liquid-ice or salt-water ice at subzero temperatures, which is one of the most efficient way of chilled storage. A comprehensive study is needed to identify freshness and quality indicators of shrimp stored at zero and subzero iced, liquid-iced and salt-water iced storage.

The objectives of this study were to compare different methods to assess quality deterioration and storage stability of shrimp. The effects of chilling and superchilling storage using ice, liquid-ice or salt-water mixed with ice on quality and shelf life of shrimp were also investigated. Sensory evaluation, electronic nose measurement, chemical and microbiological analysis, along with measurements of water holding capacity of shrimp were used to evaluate the quality during storage of shrimp. The results may indicate the efficiency of quick, non-destructive tests for evaluation of shelf life of shrimp and how it is affected by storage

at different cooling conditions.

2 Material and Methods

2.1 Raw material

The Northern shrimp *Pandalus borealis* was caught in Amarfjordur (Westfjords, Iceland) on the 2nd of December in 2003, and stored in isothermic boxes containing crushed ice, followed by truck transport to the Icelandic Fisheries Laboratories. At arrival on the 4th, the temperature of shrimp was 4.5 °C. It was immediately iced with flake ice, liquid ice or salt-water mixed with ice and placed at 1.5 ± 0.4 °C and -1.5 ± 0.2 °C. The mean weight and length of the shrimp were 5.1 ± 0.6 g and 9.2 ± 0.7 cm, respectively. The initial moisture content of the shrimp was 81.1% (w/w wet basis); protein content 17.4%; fat content 0.4%; and salt content (NaCl) 0.7%. The liquid ice was supplied by Optimar (Reykjavik, Iceland) and its initial temperature was -2.1 °C, salt content 3.5% and the ice content 27% - 30%. The flake ice was made of potable water at laboratory.

2.2 Experimental design

The shrimp was randomly divided into four groups, 15 kg each group, that were kept under different cooling conditions (Table 1). Two groups were stored at 1.5 °C in flake ice (ICE/+) and liquid ice (LIQ/+). The other two groups were stored at -1.5 °C in liquid ice (LIQ/-) and in salt-water mixed with ice (S-ICE/-). The shrimp was piled in bins in thin layers with alternating layers of the cooling agent used and covered with the cooling agent. The center temperature in each bin was measured with 1 h intervals using automatic temperature loggers. Additionally, the ambient temperatures of the refrigerated chambers were monitored.

Tab.1 Experimental design for the chilled and superchilled storage of shrimp

group	type of ice	ratio of shrimp to ice	draining of ice during storage	ambient temperature	average temperature in bins
ICE/+	flake ice	1:1.5	yes	1.5 ± 0.4 °C	-0.7 ± 0.2 °C
LIQ/+	liquid ice*	1:2.9	yes	1.5 ± 0.4 °C	-1.0 ± 0.8 °C
S-ICE/-	salt water (30%)** + ice (70%)	1:1.5	no	-1.5 ± 0.2 °C	-1.3 ± 0.0 °C
LIQ/-	liquid ice†	1:2.9	no	-1.5 ± 0.2 °C	-2.5 ± 0.1 °C

Notes: * The initial temperature of the liquid ice was -2.1 °C, the salt content 3.5% and the ice content 27% - 30%; ** Salt content of the salt-water was 4%

2.3 Sampling and preparation of samples

On day 0, 1, 4 and 6 of storage, duplicate samples were taken from each group for evaluation of microbial growth, chemical content (protein, fat, water, salt), TVB-N, TMA, pH, water-holding capacity, volatile compounds with electric nose and of sensory attributes. Actually, sampling points reflected total times of 3, 4, 7 and 9 days after catch. No preparation was needed for sensory analysis and the electric nose. Analysis of TVB-N, TMA and microbes was performed after mincing the whole shrimp with shell. Measurements of water holding capacity were performed on the peeled shrimp without further preparation except for analysis of chemical content and pH, the shrimp was minced.

2.4 Chemical content and pH

Protein content in shrimp meat was determined by the Kjeldahl method^[28]. Salt content was determined using the potentiometric method^[29]. Fat content was determined by the method of AOCS Official Method Ba-3-38^[30]. Water content in shrimp meat was determined according to the method ISO 6496^[31]. Acidity (pH) was measured using a puncture, combination electrode (SE 104) connected to a pH meter (Knick-Portamess 913 pH, Berlin, Germany). The electrode was dipped into minced shrimp meat at of 20–21 °C.

2.5 Water-holding capacity

Water-holding capacity (WHC) of the peeled whole shrimp was determined by centrifugation, based on a method described by Eide and others^[32] with some modifications. Each shrimp was weighed accurately before centrifugation (average 3.5g) and immediately centrifuged at $3\,500\text{ r}\cdot\text{min}^{-1}$ for 5 min; with temperature maintained at 10 °C. The water-holding capacity expressed as: g water remaining in the shrimp after centrifugation was divided by g water in shrimp before centrifugation. Remaining water after centrifugation was determined as g water in shrimp before centrifugation minus weight lost (g) during centrifugation.

2.6 Microbial analysis

The total viable count (TVC) was performed according to the Compendium of Methods for the Microbiological Examination of Foods published by the American Public Health Association^[34]. This procedure was then followed by weighing 25 g of each

the minced sample, homogenizing it in 225g of dilution buffer. 1 ml of the primary 1/10 suspension was then withdrawn and decimal dilutions were prepared in dilution buffer. Total viable counts were done on agar containing 0.5% NaCl by pour plate and incubated at 22 °C for 72 h for psychrophilic bacteria. The conventional “pour-plate” method was used. Plates showing colony numbers of 25 to 250 were then selected for counting. The number of colonies counted thus constitutes the total viable counts (TVC).

2.7 TVB-N and TMA

Total volatile basic nitrogen (TVB-N) and trimethylamine (TMA) were determined using steam distillation in the minced shrimp tissue, followed by titration method^[34]. The TVB-N analysis was performed through direct distillation into boric acid using a Kjeldahl-type distillatory (Struer TVN). The acid was titrated with diluted H₂SO₄ solution. To determine TMA, the same method as for TVB-N was used, except that 20 mL of 35% formaldehyde were added to the distillation flask to block the primary and secondary amines, an alkaline binding mono- and di-amine, TMA being the only volatile and measurable amine^[35].

2.8 Sensory evaluation

A Quality Grading Scheme was used to evaluate the quality of the whole shrimp (Table 2). Duplicate samples were taken after 0, 1, 4 and 6 days of storage from each group and placed in 2 clean transparent glass bowls, which were coded with a random three digit number. After 20 min the assessment was carried out under room temperature and adequate fluorescent light by a trained sensory panel. The appearance and smell of the samples were evaluated, not the taste.

2.9 Electronic nose measurements

Electronic nose measurements were performed using an electronic nose called FreshSense, developed by the Icelandic Fisheries Laboratories (IFL) and Bodvaki (Maritech, Iceland)^[22]. The instrument consists of a glass container closed with a plastic lid, an aluminum sensor box fastened to the lid, and a personal computer running a measurement program. The measurement technique was reported earlier by Olafsdottir *et al.*^[23]. A 500 g shrimp was analyzed each time; the measurement time was 5 min and temperature was 7–9 °C.

Tab. 2 Score sheet for quality grading scheme of whole shrimp

score/grade	description
5 excellent	colour is dark red to bright pink. roes are blue-green (copper). strong seaweedy, marine odour
4 good	colour is natural light pink. roes are blue-green (copper). weak characteristic shrimp odour
3 moderate	marine/shrimp odour is diminishing, weak "fishy odour", even slight ammonia. colour is natural light pink with grey-greenish or yellowish discoloration. roes are light green
2 borderline-clearly not fresh	weak ammonia odour. colour is natural light pink with grey-greenish or yellowish discoloration. roes are discoloured. blackening on the head can be spotted unfit spoiled ammonia odour. colour is natural light pink with grey-greenish or yellowish discoloration. roes are dark. blackening on the head is extensive. spoiled odour

Notes: Tab. 2 referred[36]

3 Results and Discussion

3.1 Water-holding capacity (WHC)

The water-holding capacity of the shrimp after storage was lower than that for the raw shrimp before storage (Fig. 1). It decreased relatively more during the first day, than the rest of the storage period, especially for the shrimp stored in ice. The WHC decreased at higher rate from day 1 to 6, in the shrimp stored in liquid ice at -1.5°C than in other groups.

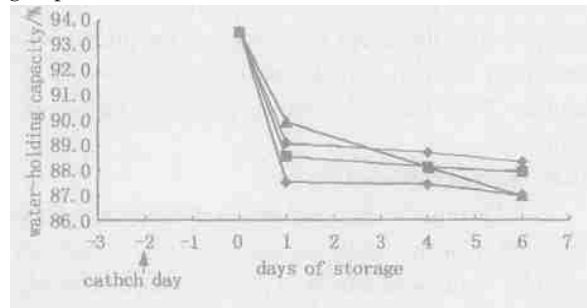


Fig. 1 Changes of water-holding capacity of shrimp stored in different conditions during the storage period

ICE/+ : flack ice at 1.5°C ; LIQ/+ : liquid ice at $+1.5^{\circ}\text{C}$; S-ICE/- : salt-water + ice -1.5°C ; LIQ/- : liquid ice at -1.5°C

3.2 Microbial analysis

Initial TVC of the shrimp was $2.4 \times 10^5 \text{ cfu} \cdot \text{g}^{-1}$ (Fig. 2). After one day of storage, a decrease in bacterial total numbers to $7.2 \times 10^4 \text{ cfu} \cdot \text{g}^{-1}$ and $2.0 \times 10^5 \text{ cfu} \cdot \text{g}^{-1}$ was observed, in the two groups stored in liquid ice at -1.5°C and 1.5°C respectively. After storage of 6 days, the values had increased to $1 \times 10^6 \text{ cfu} \cdot \text{g}^{-1}$ and $1.7 \times 10^7 \text{ cfu} \cdot \text{g}^{-1}$, respectively.

In shrimp stored in ice at 1.5°C and salt-water mixed with ice at -1.5°C , the TVC increased steadily during storage. The microbiological growth rate was faster in the shrimp stored in ice at 1.5°C than in the other three groups during the storage period.

The TVC increased from a initial level of $2.4 \times 10^5 \text{ cfu} \cdot \text{g}^{-1}$ to $3 \times 10^8 \text{ cfu} \cdot \text{g}^{-1}$ at the end of storage period. In the shrimp stored in salt water mixed with ice, it was $6.4 \times 10^7 \text{ cfu} \cdot \text{g}^{-1}$ after storage.

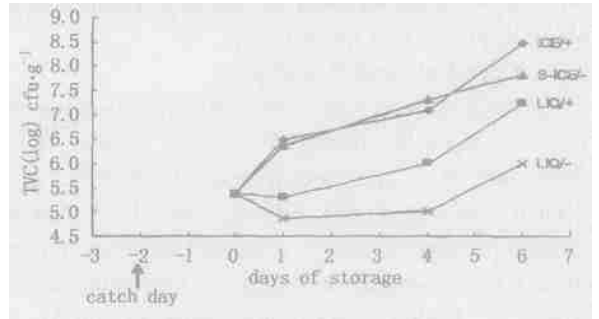


Fig. 2 Changes in total viable counts (TVC) in shrimp during storage

ICE/+ : flack ice at 1.5°C ;
LIQ/+ : liquid ice at $+1.5^{\circ}\text{C}$; S-ICE/- : salt-water + ice -1.5°C ; LIQ/- : liquid ice at -1.5°C

The initial reduction in the total bacteria in shrimp stored in liquid ice can be explained because of cold shock^[37]. The growth was first resumed after a lag phase of at least 24 h, and the slowest bacterial growth was found in the sample stored in liquid ice at -1.5°C compared to other groups. The results are in good agreement with the report presented by Lakshmanan and others^[4].

The extension of shelf-life of the shrimp stored in liquid ice at -1.5°C was attributed to delayed microbial growth. Other reports have shown that liquid ice can flow freely and surrounds the entire sample resulting in rapid cooling and less damage of the samples^[38].

3.3 TVB-N and TMA

Total volatile basic nitrogen (TVB-N) value of $33.5 \text{ mg} \cdot 100\text{g}^{-1}$ whole shrimp was found at the beginning of storage (Fig. 3). The high initial value of TVB-N was due to the following factors: the first one is that not enough ice was present to maintain constant temperature during the transportation period.

The second one, which may be the main factor, is that the high TMA formation by amino acids deamination or by decomposed from TMAO. The third is that the presence of putrescine-and cadaverine-forming bacteria in shrimp can grow at 0°C and contribute to amine formation^[4].

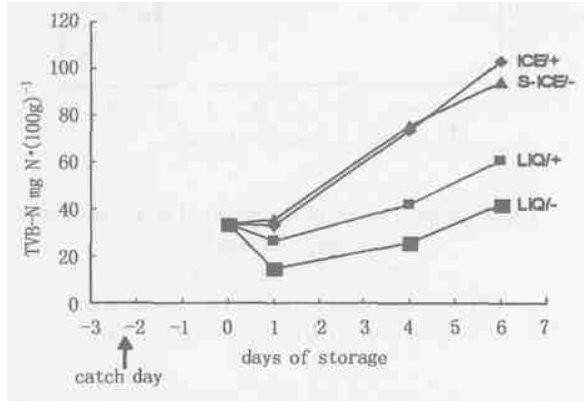


Fig. 3 Total volatile basic nitrogen (TVB-N) formation of shrimp stored in different conditions during 6 days storage period
ICE/+ : flack ice at 1.5°C; LIQ/+ : liquid ice at + 1.5°C;
S-ICE/-: salt water+ ice - 1.5°C;
LIQ/-: liquid ice at - 1.5°C

The rate of increases of TVB-N in shrimp stored in liquid ice was slower than the other two groups stored in ice or salt-water ice. After 1 day storage lower values were observed for the TVB-N and a delay in the onset of TVB-N production in the groups stored in liquid ice (LIQ/- or LIQ/+). Especially for the group LIQ/-, showing the lowest TVB-N levels on day 1 of storage and a longer lag phase before resuming increases. However in the other two groups, ICE and S-ICE/-, the TVB-N value increased to more than 70 mg · 100g⁻¹ on the fourth day of storage. The results suggest that the growth of the main spoilage causing microorganism was restrained by the liquid ice. Similar results were shown by the bacteria measurements (Fig. 4).

Initial trimethylamine (TMA) value of the sample was 0.5 mgN · 100g⁻¹ on day 0 when the shrimp arrived at laboratory, 2 days after catch, TMA formation gradually increased over the storage period with the exception of liquid ice group (LIQ/-) at lower ambient temperature (-1.5°C). In that group, TMA was reduced to 0 mgN · 100g⁻¹ on day 1 and after a lag phase, TMA began to increase after

day 4. A comparison of the rates of TMA formation during 6 days of storage revealed that shrimp stored in salt-water mixed with ice (S-ICE/-) and shrimp stored in ice (ICE/+), in which TMA values exceeded 10 mgN · 100g⁻¹, spoiled earlier than other two groups where TMA level remained below 10 mgN · 100g⁻¹ until on day four of storage. In addition, the extent of increase in TVB-N and TMA in shrimp stored in liquid ice at 1.5°C was considerably smaller than for sample groups stored in ice or in salt water mixed with ice (S-ICE/-, ICE/+).

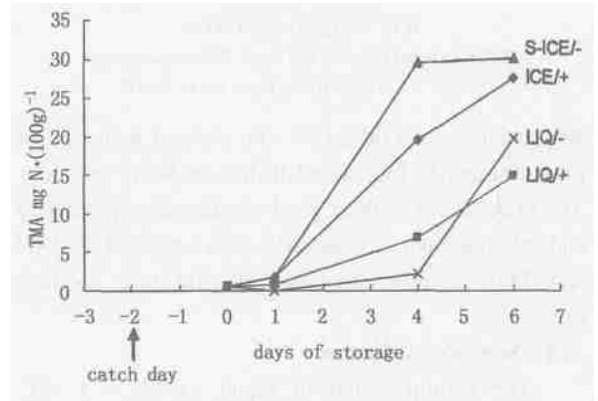


Fig. 4 Trimethylamine (TMA) formation of shrimp stored in different conditions
ICE/+ : flack ice at 1.5°C;
LIQ/+ : liquid ice at + 1.5°C; S-ICE/-:
salt water + ice - 1.5°C; LIQ/-: liquid ice at -1.5°C

The high initial levels of TMA and TVB-N may be explained by relatively high tissue enzyme activity in Northern white shrimp (*Penaeus setiferus*), which can rapidly produce ammonia during post-mortem or during the early stages of ice storage.

3. 4 Changes in pH of the shrimp

The initial pH of the shrimp was 7.41 upon its arrival. The increases of pH value were rapid in sample stored in ice at 1.5°C, and reached the final pH of 8.26 (Fig. 5). However, the changes were small in samples stored in liquid ice at -1.5°C, the pH was 7.98 at the end of storage.

Significant differences ($P < 0.05$) were noticed from the results of statistical analysis. There was a continued increase in pH for all sample groups, probably due to amines formation by amino acids decarboxylation^[15] and because of the formation of alkaline compounds produced by the metabolism of the microorganisms^[18]. This is in good agreement with

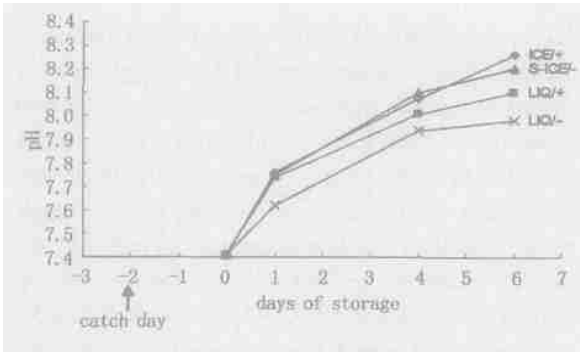


Fig. 5 Changes of pH value of the shrimp stored in different conditions

ICE/+ : flack ice at 1.5°C;

LIQ/+ : liquid ice at + 1.5°C; S-ICE/-: salt-water + ice - 1.5°C; LIQ/-: liquid ice at - 1.5°C

Krishnakumar and others^[39] who showed reduction of total nitrogen in fish stored in ice sea-water and ice. The pH changes showed good correlation with sensory and microbiological results. It also reflected TVB-N and TMA accumulation and indicated the spoilage progress.

3.5 Sensory evaluation

The shrimp stored in liquid ice at - 1.5°C scored higher than other lots throughout a 6-day storage period ($P < 0.05$), which had a longer shelf life. The lowest score was awarded to shrimp stored in ice at 1.5°C and in salt-water mixed with ice at - 1.5°C, throughout the storage (Fig. 6). The rejection time of storage for acceptability was ICE/+ = 3.7 days, LIQ/+ = 4.7 days, S-ICE/- = 3.9 days, LIQ/- = 8.3 days, according to the quality grading scheme (Tab. 2). The sensory scores decreased linearly with storage time and the linear equations and correlation coefficients are as follows:

ICE/+ group, $y = -0.5258x + 3.9849$, $R^2 = 0.95$;

LIQ/+ group, $y = -0.47x + 4.20$, $R^2 = 0.95$;

S-ICE/- group, $y = -0.57x + 4.21$, $R^2 = 0.97$;

LIQ/- group, $y = -0.30x + 4.48$, $R^2 = 0.96$.

The shrimp stored in liquid ice at - 1.5°C (LIQ/-) had the slowest spoilage rate (slope value 0.30) and changes during the first 24 h, were not significant. Contrasting results were found in other groups. Moreover, increasing differences ($P < 0.05$) were evident between LIQ/- and other groups with storage time. The shrimp stored in salt-water mixed with ice (S-ICE/-) appeared to have the fastest spoilage rate (slope value 0.57). This is similar to the result shown by TMA, CO and NH₃ responses of

electronic nose measurement.

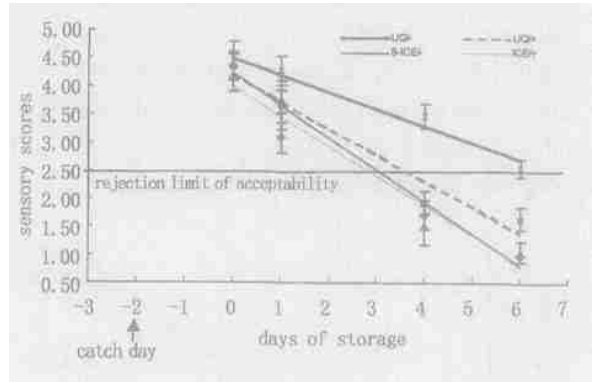


Fig. 6 Sensory scores of shrimp stored under different cooling conditions

ICE/+ : flack ice at 1.5°C;

LIQ/+ : liquid ice at + 1.5°C; S-ICE/-: salt-water + ice - 1.5°C; LIQ/-: liquid ice at - 1.5°C

The shrimp stored in liquid ice at - 1.5°C had overall higher score that means higher quality or slower spoilage rate than other groups throughout a 6-day storage period, although some assessors reported a little lower characteristic colour as a result of a slightly lighter appearance.

3.6 Electronic nose FreshSense measurements

The responses of CO and NH₃ sensors were highest and most sensitive among all the sensors of electronic nose measurement for the sample stored under different conditions (Fig. 7, 8). The responses of H₂S and SO₂ sensors were not accounted for in the report due to their low responses towards all the sample groups during storage. This indicates that the development of sulfur compounds dose appear to be of importance during storage of shrimp under these conditions.

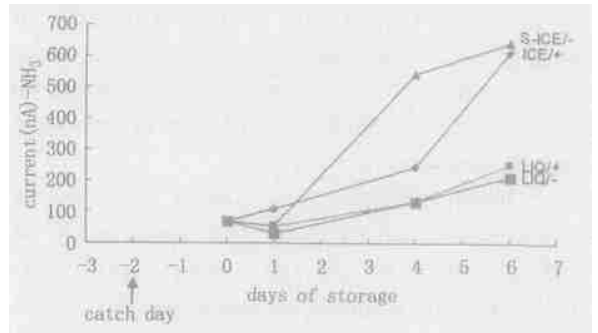


Fig. 7 Responses of NH₃ sensors to the shrimp stored in different conditions

ICE/+ : flack ice at 1.5°C;

LIQ/+ : liquid ice at + 1.5°C; S-ICE/-: salt-water + ice - 1.5°C; LIQ/-: liquid ice at - 1.5°C

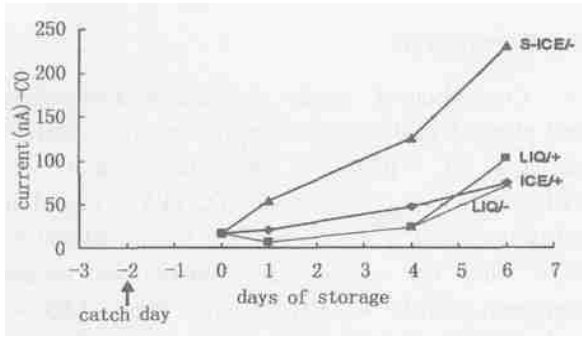


Fig. 8 Responses of CO sensors to the shrimp stored in different condition
 ICE/+ : flack ice at 1.5°C;
 LIQ/+ : liquid ice at + 1.5°C; S-ICE/-: salt-water + ice - 1.5°C; LIQ/-: liquid ice at - 1.5°C

The results indicate that response of NH_3 sensor of the electronic nose can be used to evaluate the shrimp quality as TVB-N, TMA and TVC because of existing good correlation between NH_3 sensor of the electronic nose and TVB-N ($R=0.94$), TMA ($R=0.94$), and TVC ($R=0.86$). The rapid onset of NH_3 production and high initial TVB-N in shrimp seem to be in accordance with earlier reports that the amine-forming bacterial population in fresh shrimp was slightly higher ($10^2 \text{ cfu} \cdot \text{g}^{-1}$) than in fish^[4].

The fact that the NH_3 sensor shows a sensitive

response during the first day of storage demonstrates that the electronic nose can be applied to indicate the quality change of shrimp. Olafsdottir and others^[22,23] reported that the NH_3 response of electronic nose measurement gave the best prediction to TVB in capelin raw material and was similar to the information provided by TMA for redfish.

The CO response showed lower responses, but similar trends in responses for all the storage groups as for the NH_3 sensor, except for the group stored in ICE/+ (Fig. 8). The CO response did not show that quality spoilage quickly occurred in shrimp stored in ice. This was not in accordance with results from other indicators that were TVC, TVB-N and TMA in the trial.

3.7 Principal component analysis

The data from various measurements used to monitor quality in shrimp stored under different cooling conditions were analyzed by principal component analysis (PCA) as shown in Fig. 9. The purpose was to study the main trend in the data and to illustrate the effect of the different storage types on the quality and spoilage level of shrimp. The results should indicate if the various analytical techniques applied were comparable to evaluate quality.

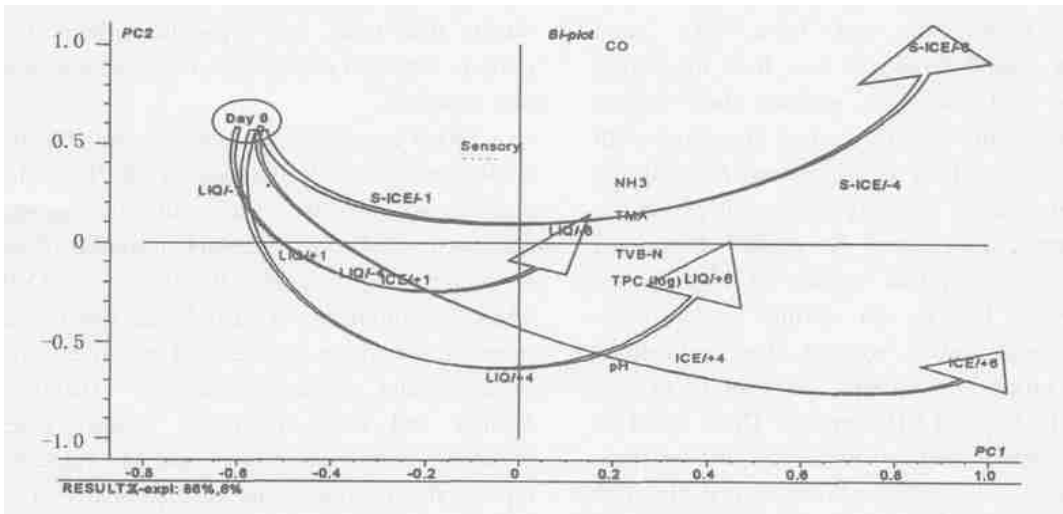


Fig. 9 Bi-plot for PCA of measured main data

Scores are labeled with the storage condition and days of storage. Loadings of variables include TVB-N, TMA, TVC, pH, sensory score and FreshSense measurements (CO and NH_3). ICE/+ : flack ice at 1.5°C; LIQ/+ : liquid ice at + 1.5°C; S-ICE/-: salt-water + ice- 1.5°C; LIQ/-: liquid ice at - 1.5°C

Fig. 9 shows the PCA scores and loadings plot of all samples and data from TVB-N, TMA, TVC, pH, sensory scores and CO, NH₃ response of electronic nose FreshSense measurement. The X-axis is the first principal component (PC1) that explains 86% of the variance in the data set and PC2 explains 6%. It can be seen that the first PC1 represents the spoilage level of the sample with the increasing storage time from left to right along PC1. Group ICE/+ 6 and S-ICE/- 6, even ICE/+ 4 and S-ICE/-4 are located in the right in the diagram, while LIQ/-6 is just located in the middle. The result indicates that the shrimp (LIQ/-) stored in liquid ice at -1.5 °C tend to spoil later than the other groups, the shrimp stored in ice (ICE/+) spoil first, and the shrimp stored in S-ICE/- spoil sooner than the others. The NH₃ response, TMA, TVB-N and TVC are located close to each other in the plot (Fig. 9), illustrating that these indicators keep high correlation and give the similar information that can indicate the quality change of the shrimp, the findings are in agreement with the results from analysis of variance (no showing data). Olafsdottir *et al.*^[22] have reported that the CO response and the QIM method are highly correlated for redfish under all storage conditions, and that the response of the NH₃ sensor and TMA measurement give similar information and have very good correlation for redfish stored in ice. It is interesting that both the CO and NH₃ sensors show higher responses towards the S-ICE/- group compared with the ICE/+ group which is in agreement with the result of TMA analysis showing higher values for the S-ICE/- group. This should be studied further in combination with microbial studies to identify the specific spoilage bacteria in shrimp under these conditions. These results suggest that metabolites from TMA producing bacteria contribute to the responses of the CO and NH₃ sensors. These could be *Pseudomonas* species that are known to also produce volatile ketones, aldehyde and esters that the CO sensor can be detected^[40]. The PCA plot shows that the loading of the CO sensor appears to contribute to the positioning of the S-ICE/- group on the upper half of the plot indicating a different spoilage pattern for that group, perhaps because of conditions that favor the growth of a different specific spoilage bacterium compared with the other groups.

4 Conclusions

Comparison of sensory, chemical, microbiological and physical quality parameters of shrimp, stored in ice at 1.5 °C (ICE/+), in liquid-ice at 1.5 °C (LIQ/+), in liquid-ice at -1.5 °C (LIQ/-), and in salt-water ice at -1.5 °C (S-ICE/-), showed that S-ICE/- did not extend the shelf-life of shrimp compared to ICE/+ . On the other hand, LIQ/+ and LIQ/- with the rapid cooling due to lower temperature and better covering, delayed the rate of quality deterioration and extended the shelf-life, especially LIQ/- which gave the longest shelf-life.

Application of liquid ice storage decreased the rate of TVB-N and TMA formation and delayed the growth of microorganism compared to salt-water iced or iced storage. Rate of production of both TVB-N or TMA and total viable counts (TVC) in shrimp stored in ice or in salt-water ice were always higher than other two groups, stored in liquid ice. The shelf-life of shrimp stored in liquid ice at -1.5 °C was extended compared to other storage conditions according to the indicators, TVB-N, TMA, pH, TVC, NH₃ response of the electronic nose and sensory evaluation. Shrimp stored in liquid ice at -1.5 °C received higher sensory score and indicated higher quality than other iced types throughout the storage period, although slight loss of the characteristic colour was observed.

Good correlation existed between the traditional quality evaluation techniques, TVB-N, TMA, TVC and sensory analysis. The results of electronic nose measurement showed that NH₃ response of electronic nose correlated well with the traditional TVB-N and TMA measurements. This indicates that the electronic nose measurements can be used effectively to monitor freshness and spoilage of shrimp. Therefore, it is feasible and efficient to use sensory assessment, electronic nose measurement and pH value to predict rapidly the freshness and quality status of Northern shrimp.

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北极虾在不同冷藏条件下的质量变化与质量指标

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摘要: 采用感官评估、物理、化学、微生物分析方法, 对贮藏在不同冷藏条件下的北极虾的质量变化与质量指标进行了研究。保藏方法分别为传统冰块冷却法、液态冰冷却法、盐水-冰混合冷却剂法, 贮藏环境温度为 -1.5°C 或 1.5°C 。研究表明, 液态冰冷藏法对延缓虾腐败变质的效果比传统冰块冷藏法、盐水-冰混合冷却剂冷藏法好。经过 1d 的贮藏后发现, 无论在 -1.5°C 还是 1.5°C 的环境温度下, 保藏在液态冰中虾的挥发性总氮(TVB-N)都有所下降, 并且在 -1.5°C 的环境温度下, 其 TVB-N 值在 3d 后才回升到刚开始贮藏时的水平, 而在其它保藏方法中, 虾的 TVB-N 值始终随贮藏时间的延长而增加; 除保藏在液态冰 -1.5°C 环境中虾的三甲胺(TMA)在贮藏的第 1 天有所降低以外, 其它各试验组虾的 TMA 值均随贮藏时间的延长而增加。检测结果还表明, 保藏在传统冰块及盐水-冰混合冷却剂中虾的细菌总数(TVC)增加最快, 其次是保藏在液态冰中 1.5°C 的环境下。而保藏在液态冰中 -1.5°C 的环境下, 虾的细菌繁殖最慢, 并且在贮藏初期, 产生了明显的细菌总数降低及细菌繁殖被抑制的现象。采用主要因子分析(PCA)和方差分析(ANOVA)发现, 质量指标如 TVB-N、TMA、TVC、pH、 NH_3 (电子鼻测量值)和感官评估结果等相互之间存在着良好的相关性。

关键词: 北极虾; 液态冰; 过冷; 电子鼻; 感官评估; 腐败

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