Quality Changes of Shrimp (*Pandalus borealis*) Stored under Different Cooling Conditions

QING ZHU ZENG, KRISTIN A. THORARINSDOTTIR, AND GUÐRUN ÓLAFSDOTTIR

**ABSTRACT:** The influence of different cooling techniques and storage temperatures (–1.5 °C or 1.5 °C) to prolong the shelf life of shrimp was evaluated by sensory analysis, physical methods, chemical analysis, and microbial analysis. Storage in liquid ice was more effective than flake ice or brine mixed with flake ice in delaying spoilage of the shrimp by slowing down microbial growth and formation of total volatile basic nitrogen (TVB-N) and trimethylamine (TMA). Total viable counts (TVC) showed that bacteria grew more quickly in shrimp stored in liquid ice and in brine mixed with flake ice, followed by those in liquid ice at 1.5 °C and –1.5 °C, respectively. TVC limits were observed in shrimp stored in liquid ice at –1.5 °C where the lag phase of growth was apparently extended at the beginning of storage. Principal component analysis (PCA) showed a good correlation between quality indicators related to microbial growth, TVC, pH, TVB-N, TMA, responses of an electronic nose and sensory evaluation.

Keywords: liquid ice, superchilling, electronic nose, sensory evaluation, spoilage

**Introduction**

The cold water shrimp (*Pandalus borealis*) is an important commercial species primarily harvested in northern areas. An estimated 70000 tonnes were landed in Newfoundland and Labrador in 2001 (FDP 2002) and 28000 tonnes in 2003 in Icelandic waters (Statistical Series 2004). Shrimp is mainly processed into frozen products in Iceland, which are primarily exported to northern Europe. Shrimp is a very perishable product, and postmortem changes occur rapidly compared with fish. The high content of free amino acids and other soluble non-nitrogenous substances, which partly contribute to the desirable, delicate sweet taste of shrimp (Kono- su and Yamaguchi 1982), can also serve as easily digestible nutrients for microbial growth. Total viable microbial counts (TVC) and chemical tests, such as analysis of trimethylamine (TMA) and total volatile basic nitrogen (TVB-N), have been used for years in the seafood industry to evaluate spoilage of seafood (Gill 1990; Botta 1995; Jackson and others 1997; Olafsdottir and Martinssdottir 1997; Oehlenschläger 1998). Limits for these quality indicators are defined in standards, guidelines, and specifications for acceptability. Similar acceptability limits have been used for shrimp as for fish. Limits of TVB-N of 30 mg N/100 g and TMA of 5 mg N/100 g in shrimp have been reported (Cobb and others 1973). However, the average TVB-N values for fresh crustaceans are often higher (Oehlenschläger 1997), and in a study by Cobb and others (1976), the initial TVB-N content of fresh shrimp tails from different batches of shrimp stored on ice ranged from 13.5 to 38.2 mg N/100 g.

Sensory evaluation using quality grading schemes are commonly used for assessment of freshness and quality in the shrimp industry. A quality grading scheme was developed by describing characteristic odor and color changes during storage of shrimp in ice and simultaneous evaluation of pH, TMA, and TVC (Martinssdot- tir 1995). Further developments in sensory schemes resulted in a QIM (quality index method) scheme for shrimp (Martinssdotir and others 1999) that has recently been reported along with QIM schemes for a number of other fish species (Luten 2000; Martinssdotir and others 2001).

An electronic nose has been used as a new rapid technique to monitor freshness and spoilage of seafood. The electronic nose has shown good correlations to TVB-N measurements and sensory analysis, for example, for capelin (Olafsdottir and others 1997, 2000), herring and fresh roe (Olafsdottir and others 1998), whole or peeled shrimp (Hognadottir 1999), and redfish (Olafsdottir and others 2002). An initial reduction in microbial load resulted after the 1st day of chilled or superchilled storage from a cold shock of the microbes (Ingram 1951; Lakshmanan and others 2002). The duration of the lag phase, the growth rate, and the composition of the microbial flora depended on the chilling method used (Cobb and others 1976; Lakshmanan and others 2002).

Jiang and Lee (1988) stated that storage in crushed ice mixed with salt (3%) resulted in higher sensory scores and lower microbial counts and TVB-N values in shrimp than when stored in pure ice. Huidobro and others (2002) showed that superchilling in liquid ice after catch slowed down microbial growth and formation of TVB-N when compared with chilling in flake ice. Riaz-Fatima and others (1988) studied sensory, biochemical, and microbiological changes in shrimp muscle at –3 °C and 0 °C. They stated that partial freezing of the products could be used to reduce biochemical changes and microbial growth. Slower spoilage rate also affected the quality of the shrimp, which was maintained longer at –3 °C than at 0 °C.

The chilling rate and final temperature of the products depend on the method applied. Soaking in chilled water (CW), ice slurry, superchilled brine (RSW = refrigerated sea water) or liquid ice provides a more uniform and rapid chilling with limited oxygen compared with chilling with flake ice. Liquid ice and RSW contain salt or other additives to lower their freezing point, which makes superchilling possible (Huss 1995). Superchilling of muscle food can result in partial freezing, which may lead to negative changes such as...
drip loss and decreased water-holding capacity (Love and Robertson 1968; Sikorski and others 1976; Robinson 1985). Changes are not only temperature dependent but are also affected by increases in ionic strength due to partial freezing and/or uptake of salt from the cooling agent when superchilled brine or liquid ice is used. Salt uptake results in lower freezing point of the fish muscle (Miles and others 1997) which parallel to increased ionic strength in the muscle has positive effects on water-binding properties (Offer and Knight 1988). Enzyme activity may increase during superchilling due to higher concentration of solubles in unfrozen water and improved access of enzymes to substrate. This may lead to negative changes in texture and taste (Fennema and others 1973; Huss 1995; Kjaersgard and Jessen 2003).

Little information is available on quality deterioration of cold water shrimp stored in liquid ice or brine and ice at subzero temperatures. This work was therefore undertaken with the objective of studying the effects of different chilling and superchilling conditions to prolong the shelf life of shrimp. Quality indicators for shrimp were evaluated by comparing results of sensory, chemical, microbiological analyses, and measurements of water-holding capacity of shrimp. Since the spoilage pattern and quality indicators may vary depending on the chilling methods used, it is important to verify the validity of the electronic nose and traditional quality methods.

Materials and Methods

Raw material

The northern shrimp (Pandalus borealis) was caught in Arnarfjordur (Westfjords, Iceland) in December 2003 and stored in isothermic boxes containing crushed ice, followed by truck transport to the Icelandic Fisheries Laboratories (IFL). Because of bad weather conditions, the transport to the laboratory was delayed. The shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch. The shrimp was immediately iced with flake ice melted during transport, and the shrimp had reached 4.5°C upon arrival 2 d after catch.

Experimental design

The shrimp was randomly divided into 4 15-kg groups and piled in bins with alternating layers of the cooling agent used (Table 1). Two groups were stored at ambient temperatures of 1.5°C, in flake ice (ICE/+), and liquid ice (LIQ/+), where melted ice was allowed to drain away. The other 2 groups were stored at ~1.5°C in liquid ice (LIQ/-) and in brine mixed with flake ice (S-ICE/-); the shrimp was kept in whole boxes so that the melted ice did not drain away.

Temperature measurements

The center temperature in each bin was measured at 1-h intervals using automatic temperature loggers (Optic StowAway®, Bourne, Mass., U.S.A.). Additionally, the ambient temperatures of the refrigerated chambers were monitored.

Sampling and preparation of samples

On days 0, 1, 4, and 6 of storage (corresponding to 2, 3, 6, and 8 d after catch), duplicate samples were taken from each group for evaluation of microbial growth, chemical content (water, salt), TVB-N, TMA, pH, water-holding capacity, volatile compounds with electronic nose, and sensory attributes. Protein and fat content were analyzed only on day 0 for characterization of the raw material. No preparation was needed for sensory analysis and the electronic nose. Analyses of TVB-N, TMA, and microbes were performed after mincing the whole shrimp with shell. Measurements of water-holding capacity were performed on the peeled shrimp without further preparation, but for analysis of chemical content and pH, the peeled shrimp was minced.

Proximate analysis and pH

Protein content in shrimp meat was determined by the Kjeldahl method (ISO 1997). Salt content in the shrimp meat was determined using a potentiometric method (AOAC 1995). Fat content was determined by the AOCs Soxhlet method Ba 3-38 (AOCS 1998) using petroleum ether (Bp. 40°C to 60°C) for extraction. Water content (g/100 g) was calculated as the loss in weight during drying at 105°C for 4 h (ISO 1983). The pH of the minced shrimp was measured using a puncate, combination electrode (DE 104, Mettler Toledo, Greifensee, Switzerland) connected to a pH meter (Knick-Porthmesser 913 pH, Berlin, Germany). The electrode was dipped into minced shrimp meat at 20°C ± 2°C.

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 (1982) with some modifications. Each shrimp was weighted accurately before centrifugation and immediately centrifuged at 1460 x g for 5 min, at 10°C. The weight loss after centrifugation was divided by the water content of the shrimp before centrifugation and expressed as %WHC.

Microbial analysis

The total viable count (TVC) was performed according to the Compendium of Methods for the Microbiological Examination of Foods (APHA 1992). Total viable counts were done on plate count agar (PCA) containing 0.5% NaCl by pour plate and incubated at 22°C for 72 h.

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. The TVB-N analysis was performed through direct distillation into boric acid using a Kjeldahl-

Table 1—Experimental conditions for the chilled and superchilled storage of shrimp

<table>
<thead>
<tr>
<th>Group</th>
<th>Type of ice</th>
<th>Ratio of shrimp to ice</th>
<th>Draining of ice during storage</th>
<th>Temperature (°C)</th>
<th>Average temperature in bins (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICE/+</td>
<td>Flake ice</td>
<td>1:1.5</td>
<td>Yes</td>
<td>1.5 ± 0.4</td>
<td>−0.7 ± 0.2</td>
</tr>
<tr>
<td>LIQ/+</td>
<td>Liquid icea</td>
<td>1:2.9</td>
<td>Yes</td>
<td>1.5 ± 0.4</td>
<td>−1.0 ± 0.8</td>
</tr>
<tr>
<td>S-ICE/-</td>
<td>Brine + iceb</td>
<td>1:1.5</td>
<td>No</td>
<td>−1.5 ± 0.2</td>
<td>−1.3 ± 0.0</td>
</tr>
<tr>
<td>LIQ/-</td>
<td>Liquid icea</td>
<td>1:2.9</td>
<td>No</td>
<td>−1.5 ± 0.2</td>
<td>−2.5 ± 0.1</td>
</tr>
</tbody>
</table>

a The initial temperature of the liquid ice was ~2.1°C, the salt content was 3.5%, and the ice content was about 30%.
b The salt content of the brine was 4%, and the ratio of brine to flake ice was 3:7.
Quality changes of chilled shrimp . . .

Table 2—Quality grading scheme of whole shrimp*

<table>
<thead>
<tr>
<th>Score/grade</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Excellent</td>
<td>Color is dark red to bright pink. Roes are blue-green (copper). Strong seaweedy, marine odor.</td>
</tr>
<tr>
<td>4 Good</td>
<td>Color is natural light pink. Roes are blue-green (copper). Weak characteristic shrimp odor.</td>
</tr>
<tr>
<td>3 Moderate</td>
<td>Marine/shrimp odor is diminishing, weak “fishy odor,” even slight ammonia. Color is natural light pink with grey-greenish or yellowish discoloration. Roes are light green.</td>
</tr>
<tr>
<td>2 Borderline—clearly not fresh</td>
<td>Weak ammonia odor. Color is natural light pink with grey-greenish or yellowish discoloration. Roes are discolored. Blackening on the head can be spotted.</td>
</tr>
<tr>
<td>1 Unfit spoiled</td>
<td>Ammonia odor. Color is natural light pink with grey-greenish or yellowish discoloration. Roes are dark. Blackening on the head is extensive. Spoiled odor.</td>
</tr>
</tbody>
</table>


Sensory evaluation

A quality grading scheme that is commonly used in the shrimp processing in Iceland was used to evaluate the quality (Table 2) (Martinsdóttir and others 1995). The appearance and smell of the samples were evaluated, not the taste. Duplicate samples of 150 g were taken after 0, 1, 4, and 6 d of storage from each group and placed in 2 transparent glass bowls, which were coded with a random 3-digit number. After 20 min, the assessment was carried out in a pilot kitchen at room temperature (20 °C) and adequate fluorescent light with 10-min intervals between duplicates. Sensory assessments were carried out by 6 to 9 assessors (age range, 25 to 65 y), both female and male. They were all trained according to international standards (ISO 1993), for evaluation of different seafood, including detection and recognition of tastes and odors by use of scales and descriptors.

Electronic nose measurements

Electronic nose measurements were performed using an electronic nose, FreshSense, developed by the IFL and Bodvaki (Maritech, Iceland) (Olafsdóttir and others 2002). The instrument was based on 4 electrochemical sensors (Dräger, Lübeck, Germany: CO, H₂S, and SO₂; City Technology, Portsmouth, Britain: NH₃) and a closed glass sampling vial (2.3 L). The headspace of the samples was circulated from the sampling vial to the sensor chamber by a pump. Data acquisition and recording were done by a personal computer with a Labview measurement program. The measurement technique and the accuracy of the measurements were reported earlier by Olafsdóttir and others (2000, 2002). About 500 g of shrimp were analyzed each time; the measurement time was 5 min, and the temperature of samples was 7 °C to 9 °C.

Statistical analysis

Statistical analysis was performed by Microsoft Excel 8.00 (Microsoft Inc, Redmond, Calif., U.S.A.) and NCSS 2000 (NCSS, Kaysville, Utah, U.S.A.). Multivariate analysis of the data (principal component analysis) was performed in the statistical program Unscrambler (Version 7.5, CAMO ASA, Oslo, Norway). Principal component analysis (PCA) is a tool, based on statistics, for identifying relationships in complex analytical data by comparing data in more than 1 dimension. The main objective was to detect structure in the relationship between measured variables and experimental factors. Average of sample replicates were used for each sample. All the data were mean centered and scaled to equal variance before PCA. Cross-validation was used in the validation method.

Results and Discussion

Temperature profiles during storage

The cooling rate of shrimp was more rapid in liquid ice than in flake ice and in brine mixed with flake ice (Figure 1). The liquid ice formed a more uniform cooling solution than the flake ice and therefore, the cooling capacity of the liquid ice was higher as seen by lower temperature in the bins than in the environment (–1.5 °C). However, after 3 d, the temperature of the shrimp in liquid ice stored at +1.5 °C had reached about –0.5 °C or similar to the temperature of the shrimp stored in ice. After 3 d, the temperature still increased because of faster melting of the liquid ice than the flake ice. Unfortunately, the temperature was only monitored for 4 d until samples reached the sensory rejection limit; therefore, no temperature data are available for the last 2 d. The temperature of the superchilled shrimp stored in liquid ice was the same (–2.6 °C) during the 4-d storage period. However, temperature fluctuations were observed on day 4, and it is likely that the temperature may have increased during the last 2 d of the experiment. It is also likely that the temperature of the shrimp stored at 1.5 °C may have continued to increase to reach the environmental temperature. On the other hand, the temperature of shrimp stored in brine mixed with flake ice was the same (–1.3 °C) during the 4 d. It may have remained the same during the last 2 d because it was close to the storage temperature (–1.5 °C).

Figure 1—Changes in temperature (°C) of shrimp during chilled and superchilled storage. ICE/+ = flake ice at 1.5 °C; LIQ/+ = liquid ice at +1.5 °C; S-ICE/+ = brine mixed with flake ice –1.5 °C; LIQ/- = liquid ice at –1.5 °C.
Chemical analysis and water-holding capacity

The initial moisture content of the shrimp was 81.1%, protein content was 17.4%, fat content was 0.4%, and salt content (NaCl) was 0.7%. During storage, the salt in shrimp stored in liquid ice at –1.5 °C increased to 2.2% during the 1st day of storage and increased further to 2.5% after 4 d (Figure 2). The salt content remained similar in other groups except a slight decrease was observed in the shrimp stored in ice at 1.5 °C. There was an increase in salt content in the group stored in brine mixed with flake ice at –1.5 °C. However, the ice did not melt as much as the liquid ice and the brine tended to drain to the bottom of the bin, but the liquid ice formed a uniform solution surrounding the shrimp. This also explained the difference in the temperature of the different storage groups at –1.5 °C.

Water content increased in all groups during storage from 81.1% up to 85% to 85.6%. This was in agreement with previous studies of Wilaichon and others (1977) who observed an increase in water content during ice storage. When water content was calculated as the ratio of salt-free dry matter, it was observed that this ratio was about 1 to 2 units higher in the group stored in liquid ice at –1.5 °C than in the other groups (Figure 3). This showed a difference in water uptake of the shrimp muscle as a result of increased salt content, but sodium chloride has been known to increase swelling and the ability of the muscle to take up and retain water (Offer and Knight 1988; Fennema 1990). In general, water-holding capacity decreased with time, relatively more on the 1st day, than during the rest of the storage period, especially for the shrimp stored in ice. The water-holding capacity of the superchilled shrimp in liquid ice was highest after 1 d of storage but decreased more with storage time than in other groups (Figure 4). This could be explained because the ratio of loosely bound water in the muscle may have increased parallel to the brine uptake rather than because of partial freezing. As previously mentioned, the temperature of the shrimp stored in liquid ice at –1.5 °C was about –2.5 °C. The estimated freezing point of the fresh shrimp has been reported to be –2.2 °C (Rahman and Driscoll 1994). However, the freezing point was lowered by salt uptake from the liquid ice due to higher salt concentration in the muscle (Miles and others 1997).

Microbial analysis

The microbial quality of the shrimp was marginal (2.4 × 10⁵ colony-forming units [CFU]/g) at the onset of the experiment because the cooling was not efficient during transport, but the acceptable limits in the fish processing is (1 × 10⁶ CFU/g). In the shrimp stored in ice at 1.5 °C and brine mixed with flake ice at –1.5 °C, the TVC increased steadily during storage. The microbial growth rate was faster in the...
shrimp stored in ice at 1.5 °C than in the other 3 groups during the storage period. The TVC increased from an initial level of $2.4 \times 10^5$ CFU/g to $3 \times 10^8$ CFU/g at the end of storage period. In the shrimp stored in salt water mixed with ice, the TVC value was $6.4 \times 10^6$ CFU/g at the end of the storage time (Figure 5).

Storage in liquid ice delayed microbial growth and a lag phase of at least 24 h was observed. The slowest bacterial growth was found in the sample stored in liquid ice at –1.5 °C (LIQ/–). After 1 d of storage, a decrease in TVC to $7.2 \times 10^4$ CFU/g and $2.0 \times 10^5$ CFU/g was observed, in the 2 groups stored in liquid ice at –1.5 °C and at 1.5 °C, respectively. After storage of 6 d, the values had increased to $1 \times 10^6$ CFU/g and $1.7 \times 10^7$ CFU/g, respectively. The results indicated an inhibitory influence of liquid ice and superchilling on microbial growth.

The initial reduction in the total bacteria in shrimp stored in liquid ice has been explained because of cold shock (Ingram 1951; Lakshmanan and others 2002). Other reports have shown that the ability of liquid ice to flow freely and surround the entire sample resulted in more rapid cooling and less damage of the samples than when flake ice was used (Huidobro and others 2002).

**TVB-N and TMA**

The total volatile basic nitrogen (TVB-N) value was 33.5 mg/100 g in the whole shrimp at the beginning of storage (Figure 6), but the acceptability limit for shrimp has been reported to be 30 mg/100 g. However, these limits may be questionable for shrimp because higher levels have been found even in fresh shrimp (Cobb and others 1976). The high initial TVB-N was in agreement with the high microbial load, detected on the 1st day of sampling. This was explained by delays in the transport of the raw material and because not enough ice was present to maintain low temperature during the prolonged transport period. The high TVN value may also be explained because too little ice had been used, and the effects of washing out of TVN were minimized (Cobb and others 1976).

The rate of increases of TVB-N in shrimp stored in liquid ice was slower than in the other 2 groups stored in ice or brine mixed with ice. After 1 d 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, which may partly have been due to leaching of TVB-N into the brine (Cobb and others 1976). In the other 2 groups, ICE/+ and S-ICE/–, the TVB-N value increased to more than 70 mg/100 g on the 4th day of storage. The results suggest that the growth of the main spoilage causing microorganism was restrained by the liquid ice and the low temperature storage. Similar trends were observed for bacteria (Figure 5).

Initial trimethylamine (TMA) value of the shrimp was 0.5 mg N/100 g when the shrimp arrived at the laboratory 2 d after catch (Figure 7). The results showed that liquid ice delayed TMA formation compared with the other storage conditions. In the liquid ice group (LIQ/–) stored at lower temperature (–1.5 °C), an extended lag phase was observed until day 4, and the TMA level remained below the 5 mg N/100 g acceptability limit (Cobb and others 1976). The TMA values were highest for the group stored in brine mixed with ice (S-ICE/–). Earlier studies on capelin stored in CSW (chilled seawater) compared with similar capelin held in ice have shown an increased spoilage rate in the CSW system compared with storage in ice (Shaw and Botta 1975; Olafsdóttir and others 2000). In general, low temperature will inhibit the microflora, but if the cooling is not ensured, for example when the ice has melted in the chilling system, the microflora may be more active in the spoilage process. The availability of nutrients that have leached from the fish into the cooling liquid can further stimulate the growth of the bacteria.

![Figure 6](https://example.com/figure6.png)  
**Figure 6**—Total volatile basic nitrogen (TVB-N) (mg N/100 g) formation of shrimp during chilled and superchilled storage. ICE/+ = flake ice at 1.5 °C; LIQ/+ = liquid ice at +1.5 °C; S-ICE/– = brine mixed with flake ice at –1.5 °C; LIQ/– = liquid ice at –1.5 °C.

![Figure 7](https://example.com/figure7.png)  
**Figure 7**—Trimethylamine (TMA) (mg N/100 g) formation of shrimp during chilled and superchilled storage. ICE/+ = flake ice at 1.5 °C; LIQ/+ = liquid ice at +1.5 °C; S-ICE/– = brine mixed with flake ice at –1.5 °C; LIQ/– = liquid ice at –1.5 °C.

![Figure 8](https://example.com/figure8.png)  
**Figure 8**—Changes of pH value of shrimp during chilled and superchilled storage. ICE/+ = flake ice at 1.5 °C; LIQ/+ = liquid ice at +1.5 °C; S-ICE/– = brine mixed with flake ice at –1.5 °C; LIQ/– = liquid ice at –1.5 °C.
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**pH measurements**

The initial pH of the shrimp was 7.41 upon arrival. The increases of pH value were rapid in the sample stored in ice at 1.5 °C and reached a final pH of 8.26 (Figure 8). Changes in pH were slowest in samples stored in liquid ice at −1.5 °C and reached a value of 7.98 at the end of storage. The pH changes showed good correlation with sensory and microbiological results and reflected similar trends in the spoilage progress as the TVB-N and TMA measurements.

**Sensory evaluation**

The lowest sensory scores were given to shrimp stored in ice at 1.5 °C and in brine mixed with ice at −1.5 °C (Figure 9). The shrimp stored in liquid ice at −1.5 °C received the highest sensory scores, indicating higher quality or slower spoilage rate than in other groups throughout the storage period. This was in accordance with the lag phase observed for TVC, TVB-N, and TMA. However, some assessors reported a little lower characteristic color as a result of a slightly lighter appearance. Similar effects were stated by Huidobro and others (2002). The shelf life of the different sample groups was as follows: ICE/+ = 3.7 d, LIQ/+ = 4.7 d, S-ICE/− = 3.9 d, and LIQ/− = 8.3 d, according to the quality grading scheme and a sensory score of 2 as the limit of acceptability (Table 2).

**Electronic nose measurements**

The electronic nose sensors are sensitive toward different classes of compounds that form as a result of microbial activity on the muscle. The CO sensor detects mainly alcohols, aldehydes, and esters; the NH3 sensor responds only to amines, and the H2S and SO2 sensors detect sulfur compounds (Olafsdottir and others 2002). The responses of the NH3 (Figure 10) and CO (Figure 11) sensors were the highest and most sensitive of the 4 sensors of the FreshSense electronic nose. The responses of H2S and SO2 sensors showed very low responses toward all the sample groups during storage (data not shown). This indicates that the development of sulfur compounds appear not to be of importance during storage of shrimp under these conditions. Therefore, these sensors were not considered useful for monitoring spoilage of shrimp.

The NH3 sensor had the highest responses, showing the importance of amine formation in shrimp during storage (Cobb and others 1996). This is in agreement with earlier results suggesting that the NH3 sensor of the electronic nose could be used as a rapid technique to predict shrimp quality (Olafsdottir and others 1998). The NH3 sensor showed a good correlation with TVC ($r = 0.86$), TVB-N ($r = 0.94$), and TMA content ($r = 0.94$). Similarly, Olafsdottir and others (1997, 2002) showed that the NH3 response of the electronic nose gave the best prediction to TVB-N in capelin raw material and correlated well with TMA content in redfish. The high NH3 sensor responses initially coincide with the high TVB-N and TVC values in the shrimp. The NH3 sensor showed higher responses toward the S-ICE/− group compared with the ICE/+ group, which was in agreement with the result of TMA analysis showing higher values for the S-ICE/− group. Similarly, the CO sensor had the highest responses for the S-ICE/− group, indicating high levels of alcohols, aldehydes, or esters. The presence of these metabolites suggests the growth of specific spoilage organisms such as *Pseudomonas* species (Huss 1995; Gram and Huss 1996). Oxygen may not have been limiting as in LIQ/− because the brine in S-ICE/− drained to the bottom, allowing the growth of *Pseudomonas* species (Chinnivasagam and others 1998). Further studies on the role of specific spoilage organisms are needed to verify their contribution to the formation of these volatiles.

The CO sensor showed, in general, lower responses than the NH3 sensor, but similar trends for all the storage groups. An exception...
from this was the group stored in ice at 1.5 °C, which showed less increase from day 4 to day 6 than the other groups (Figure 11). This is difficult to explain but may be because water-soluble compounds can possibly leak from the fish when stored in ice if samples are drained (Magnúnsson and Martinsdóttir 1995).

**PCA (principal component analysis)**

The main trend in the data was studied by PCA to illustrate the effect of the different storage types on the quality and spoilage level of shrimp and to show the contribution of the various analytical techniques to evaluate quality. The 1st principal component (PC1) explaining 68% of the variation appeared to be expressing the spoilage level of the sample with the increasing storage time from left to right along PC1 (Figure 12). The measured variables TVB-N, TMA, TVC, pH, sensory scores, and CO and NH₃ response of the electronic nose were highly correlated as seen by their positioning on the right side on the plot. The order of the sampling groups from left to right indicates their spoilage level, and the ICE/+ group is located farthest to the right on the plot in accordance with its highest spoilage level.

The second principal component (PC2) explained 19% of the variation of the data and contributes to the differentiation of the storage groups, related to salt, water uptake, and water-holding capacity. Loadings for salt content and water uptake (w/d = water/salt-free dry material) located on the upper part of the plot were positively correlated and contributed to the discrimination of the liquid ice group stored at −1.5 °C with the highest salt content.

Bi-plot of the 1st and 3rd principal component showed that the loadings of the CO sensor, salt, and water-holding capacity discriminated the S-ICE/− group from the other groups (Figure 13) located in liquid ice and indicated a different spoilage pattern in this group as seen by high TMA values, and in particular high responses of the CO sensor.

Comparison of sensory, chemical, microbiological, and physical quality parameters of shrimp showed that S-ICE/− did not extend the shelf life of shrimp compared with ICE/+. On the other hand, the application of liquid ice extended the shelf life by delaying the growth of microorganism and decreasing the rate of TVB-N and TMA formation, especially in shrimp stored in liquid ice at −1.5 °C according to the indicators, TVB-N, TMA, pH, TVC, NH₃, and CO response of the electronic nose and sensory evaluation.

**Conclusions**

The rapid cooling of shrimp stored in liquid ice and superchilling (−1.5 °C) extended the shelf life of shrimp compared with storage in brine mixed with liquid ice at −1.5 °C and storage in liquid ice and liquid ice at 1.5 °C. Traditional quality-evaluation techniques, that is, TVB-N, TMA, TVC, and sensory analysis, showed good correlation for evaluation of shrimp. The results of electronic nose measurement showed that the NH₃ response of an electronic nose correlated well with the traditional TVB-N and TMA measurements. This indicated that the electronic nose measurements could be used effectively to monitor quality changes of shrimp under these conditions.

**Acknowledgments**

This research was carried out by the 1st author in partial fulfillment of the United Nations Univ. Fisheries Training Programme (www.unuftp.is/) in Iceland in 2003-2004.

**References**

Quality changes of chilled shrimp...