

Application of Quality Index Method, Texture Measurements and Electronic Nose to Assess the Freshness of Atlantic Herring (*Clupea harengus*) Stored in Ice

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Abstract—Atlantic herring (*Clupea harengus*) is an important commercial fish and shows to be more and more demanded for human consumption. Therefore, it is very important to find good methods for monitoring the freshness of the fish in order to keep it in the best quality for human consumption. In this study, the fish was stored in ice up to 2 weeks. Quality changes during storage were assessed by the Quality Index Method (QIM), quantitative descriptive analysis (QDA) and Torry scheme, by texture measurements: puncture tests and Texture Profile Analysis (TPA) tests on texture analyzer TA.XT2i, and by electronic nose (e-nose) measurements using FreshSense instrument. Storage time of herring in ice could be estimated by QIM with ± 2 days using 5 herring per lot. No correlation between instrumental texture parameters and storage time or between sensory and instrumental texture variables was found. E-nose measurements could be used to detect the onset of spoilage.

Keywords—Herring, Quality Index Method (QIM), freshness, storage time.

I. INTRODUCTION

HERRING is an important commercial fish [1]. In recent years, Atlantic herring (*Clupea harengus*) has been one of the most caught fish species in the world [2]. Total world catch of Atlantic herring in 2002 was 1.87 million tonnes, increasing gradually and reached 2.24 million tonnes in 2006 [2]. This fat fish species is used for producing many delicacy products such as salted, kippers, marinated, canned in oil etc. [1], however there was a large proportion of herring catch went to production of meal and oil for animal feed [3]. Fish

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production does not meet the increasing demand due to human population growth and increased incomes [4]. There has been a trend to increase the proportion of herring for human consumption: from 57-64% in 1991-1993, to 74-75% in 1994-1996, and 82-86% in the 2000s of total catch in the North-East Atlantic [5].

Based on these facts, it is very important to find good methods for monitoring the freshness of the fish in order to keep the fish in the best quality for human consumption. Sensory evaluation is a very common method of freshness measuring nowadays. There has been a trend to standardize sensory evaluation to make it objective measurement [6]. The Quality Index Method (QIM) is a promising method to measure the freshness of fish, which shows to be both rapid and reliable [7]. The method was originally developed by the Tasmanian Food Research Unit in Australia [8], and has been developed further by European fisheries research institutions. QIM gives scores closed to zero for very fresh fish whereas increases the scores as the fish deteriorates [7], [9]. QIM schemes have been developed for various species of fish including Atlantic herring (*Clupea harengus*) [7], [10]. One of the unique advantages of QIM is that it can be used to estimate storage time and remaining shelf life of the studied fish species. Sveinsdóttir and others [11] found that by assessing three salmon per lot, storage time might be predicted with ± 2.0 days at 95% significant level, but examining greater number of salmon per lot might increase the precision. Larsen and others [12] reported that when using an average of the assessors' scores it is possible to predict the remaining storage life of the fish to \pm one day.

Besides sensory methods, various techniques have been developed to monitor fish freshness. Texture is an important property of fish muscle as it is a part of quality. Fish may become tough because of frozen storage or soft and mushy due to autolytic degradation [9]. Changes in texture of fish during storage have been measured by texture analyzers for several fish such as farmed salmon, cod and haddock, and some correlation with sensory texture attributes and storage time were found [11], [13], [14].

Gas sensors or "electronic noses" have been employed for the rapid detection of volatile compounds formed by the

degradation of food composition as indicators of freshness or quality [6]. An e-nose called FreshSense, developed by the former Icelandic Fisheries Laboratories (IFL) and Bodvaki Element Sensor Systems, is sensitive to the main classes of volatile compounds (alcohol, carbonyls, sulphur compounds, and amines) which accumulate because of microbial activity and lipid oxidation during storage of fish [6], [15].

The aim of this study were to apply QIM, e-nose and texture measurements to evaluate the freshness of herring stored in ice, and to find out if and how they can be used to estimate the storage time.

II. MATERIALS AND METHODS

A. Materials

A total of 164 Atlantic herring (*Clupea harengus*) from Vestmannaeyjar - Iceland (batches 1, 2, and 3) and Neskaupstadur - Iceland (batches 4 and 5) was used in this experiment. The batches were numbered successively according to the catching time. The idea of getting different batches was to have the samples of at least two different storage times at each sensory evaluation session. Batches 1 and 2 were used for training of the sensory panel only.

Fish from Vestmannaeyjar was from the South Coast of Iceland and stored in refrigerated sea water (RSW). Fish from Neskaupstadur was caught in Vopnafjardargrunnur square 613 and stored in chilled sea water (CSW). The fish had been stored for about 3-5 days in ice (from catch) in polystyrene boxes or barrels on arrival at the laboratories. On the arrival at the laboratories, fish was rechecked and put alternately with layers of flake ice into extended polystyrene boxes (EPS). Holes were made in the bottom of the boxes for the draining of melting ice. The boxes were covered with lids and stored in a chilled room at temperature 0-2 °C. Temperature inside the boxes was monitored (recorded every 30 minutes) by electronic thermometer Optic StowAway Temp WTA32 – 37+75 241028 (US PAT 5373346). The ice in boxes was checked and added if necessary every three days. Herring was stored up to 2 weeks, and samples were taken every 2-4 days for sensory analysis, texture and e-nose measurements. Day 0 is the catching day.

B. Methods

Sensory Evaluation

Prior to the experiment, a panel of 13 judges was trained during one session using QIM scheme for herring [7] with the maximum total quality index of 20 (Appendix). The judges were all employees at the IFL, had years of experience, and were trained according to ISO 1993 [16]. They were used to perform QIM, using QIM schemes frequently evaluating fish including herring. The training was to freshen up their skill in freshness evaluation of herring. Six to ten panelists participated in the sensory analysis each time. All sample observations were conducted accordingly to international standard ISO 1988 [17]. The observations were carried out always in the same room for QIM with as little interruption or

distraction as possible, at room temperature, under white fluorescent light.

A total of 48 herring was analyzed with QIM during the training and evaluation period. In training session, 10 whole fish from 2 different batches (5 fish from each batch) were used. The judges observed herring (the storage time in ice was given) and the scheme was explained to them at the same time.

For the QIM evaluation (5 sessions over 5 sampling days) 5 fish from each batch were used each time, except for day 12 of batch 4 there were 3 herring used. The samples were collected from the boxes and placed on a clean table 30 minutes before assessment. Each herring was coded with 3 random digit numbers.

Sensory evaluation of cooked herring samples using quantitative descriptive analysis (QDA) and Torry scheme was also carried out in parallel as control methods. A total of 44 herring was used in training and evaluation sessions (4 fish from each storage day). Fillets were trimmed from belly part and tail part (3-4 cm long), cut to pieces of about 2-2.5 cm long and 2-3 cm wide. Pieces were placed in aluminium boxes and cooked in the electric oven Convostar (Convotherm-German, the oven was preheated) by steam at 95-100 °C in 7 minutes. Each panellist got duplicate samples from 2 different storage days. The samples were coded with 3 random digit numbers. The results are shown in [18].

Texture Measurements

Triplicate measurements were applied for 6 fish from each batch using the Stable Micro System texture analyzer model TA.XT2i (Surrey, England) and Texture Expert program. Six fish were collected from each batch from cold room, placed to polystyrene box with ice. Fish was removed from ice right before its measurements. Each fish was measured at 3 different points along the lateral line, the first point was placed about 2-3 cm from the gillcover, and distance between two contiguous points was 2-3 cm. The results were calculated and the averages of the 3 measurements were given as a result for each fish. The tests were the Texture Profile Analysis (TPA) (3 fish) and firmness test (puncture test in compression) (other 3 fish) using Ebonite cylinder probe 10 mm in diameter (P/10) with the following parameters: Pre test speed 2.0 mm/s; speed in the sample 0.8 mm/s; past test speed 10.00 mm/s; distance 5.0 mm; force 0.98 N; time 5 s.

Electronic Nose Measurements

Triplicate measurements were performed using the FreshSense (developed by the IFL and Bodvaki Element Sensor Systems). The small sampling container of 2.3 L was used. The sensors gave responses on CO, SO₂, NH₃, and H₂S compounds. Two fish of about 650-900 g were used for each measurement (the fish were from the texture measurements). Fish was kept on the table for about 30 minutes to warm up to 8 ± 3 °C (temperature in the grills) right before measurement. Measurements were taken every 10 seconds for 5 minutes. The reported value is the average of last three measurements

of the 5-minute measurement cycle [13], [14].

Data Analysis

Microsoft Excel 2003 was used to calculate means and standard deviations for all multiple measurements and to generate graphs. Texture Expert program was used to calculate the hardness and firmness of the samples. Pearson correlation coefficients were used to see if there was any correlation between instrumental texture parameters and storage time, or between sensory and instrumental texture attributes. The correlation analysis was conducted using SPSS version 16.0. Multivariate analysis was performed by Unscrambler® 9.0 software package (CAMO A/S). Principle component analysis (PCA) was performed to study the main variance in the data set. Partial least square regression (PLS-R) was conducted to evaluate the possibility to predict storage time of QIM.

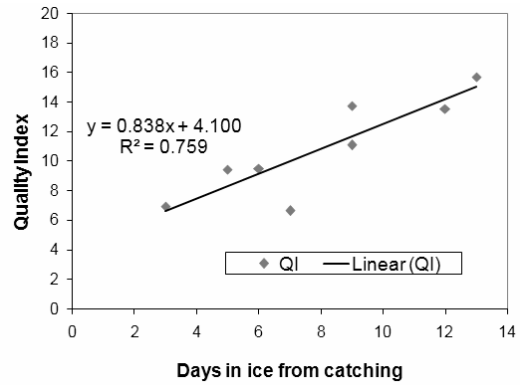


Fig. 1 Quality Index of herring stored in ice

III. RESULTS

The Quality Index (QI) was calculated for each storage day of sampling and formed a linear relationship with storage time (Fig. 1). Linear relationship between QI and days in ice was: $y = 0.838 \cdot x + 4.100$ (x - Days in ice; y - QI).

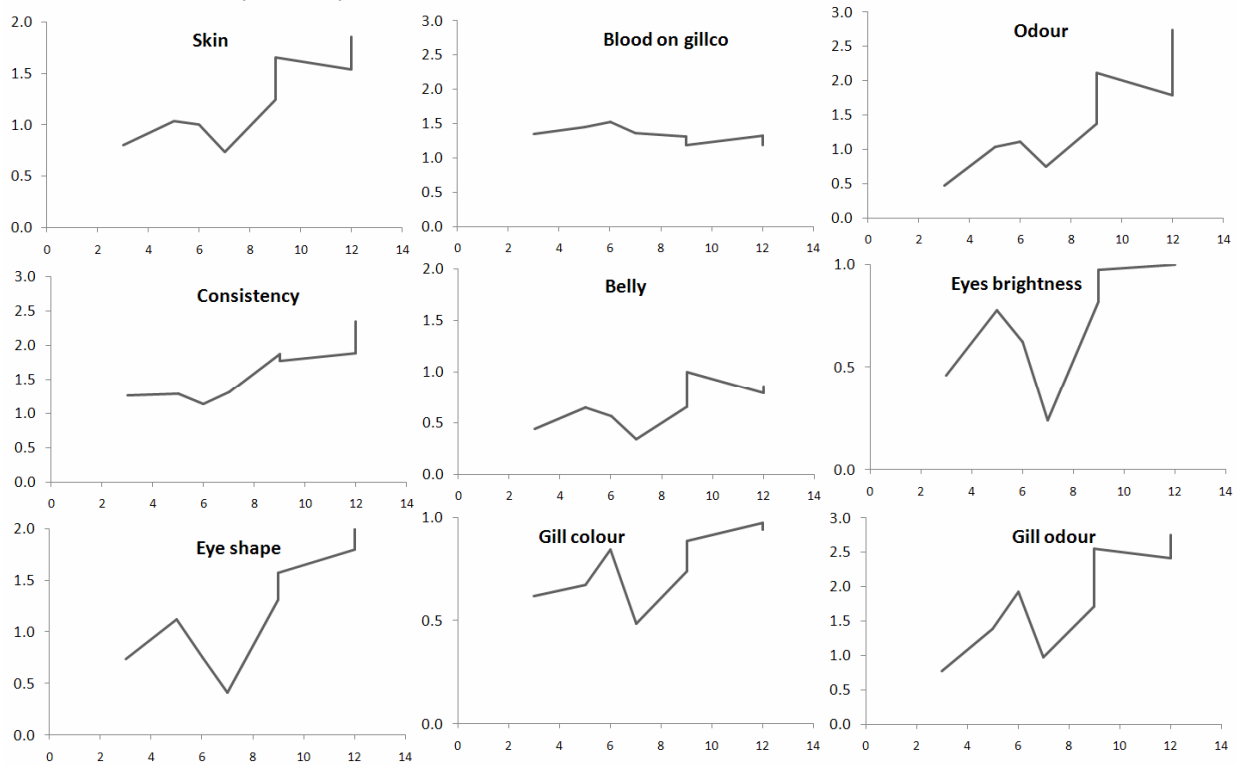


Fig. 2 Average scores of each quality attributes assessed with QIM scheme for herring against days in ice

The scores of most attributes increased with the storage time, except for day 7 (Fig. 2). The scores of the attribute “Blood on gillcover” did not increase with storage time as most attributes. This phenomenon could be also observed in Fig. 6 where other attributes clustered together with storage

time to the right side of principle component 1 (PC1) while “Blood on gillcover” was on the opposite of this PC. The scores of the attribute “Belly” (Fig. 2) were not closed to the maximum value given in the QIM scheme by the end of the storage time, i.e. 8 days based on QDA and Torry sensory

results [18]. When assessing the cooked samples after day 8, negative attributes such as off-flavour and rancid flavour (by QDA), and rancid and sour odour and flavour (by Torry scheme) were clearly detected [18]. It was difficult to distinguish the difference between days of storage (after day 8) for the QIM attribute “Gills colour” (Fig. 2). The QI did not reach its maximum score (20) even when the fish was spoilt.

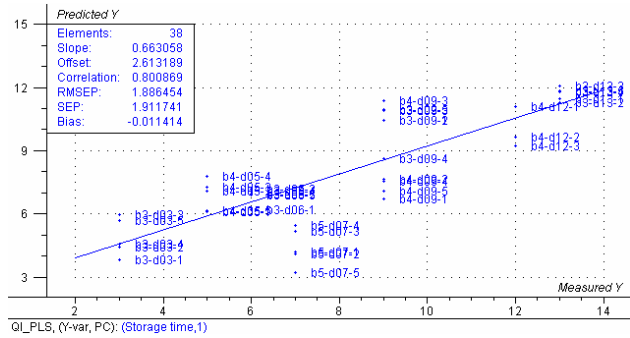


Fig. 3 PLS1 modelling of QIM data from herring stored in ice using full cross validation: predicted against measured Y values, that is storage time from catch. “b” stands for batch number and “d” for days in ice

The results were analyzed with PLS-R to examine how the QI predicted the storage time in ice of herring (Fig. 3). The standard error of performance (SEP) may be used to evaluate the precision of predictability. As QI was the sum of 9 attributes evaluated in the QIM scheme, a normal distribution can be assumed [19], therefore $2 \times \text{SEP}$ could be regarded as a 95% confidence interval [20]. So it can be assumed that the QI (if 5 herring were assessed) could be used to predict storage time with ± 2 days. Based on the value of SEP, it is advisable to use 5 herring or more from each batch in the assessment, as using fewer herring might reduce the precision of evaluation and predictability.

Hardness and cohesiveness were obtained from the texture profile analysis as the maximum force value and the ratio between the areas, respectively. Firmness was the maximum force value in the puncture test measurements. There was a high variation in the data (Fig. 4). Batch number 5 appeared to be harder, firmer than batches 3 and 4.

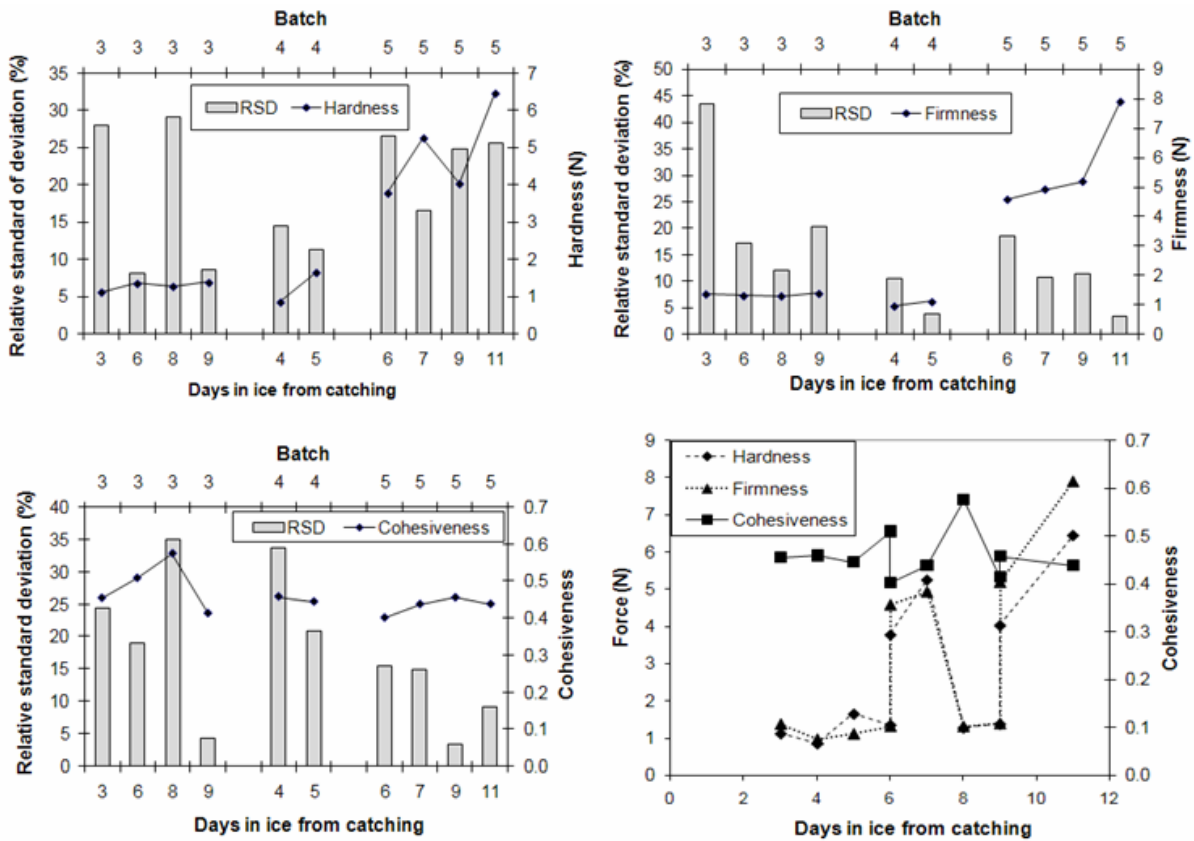


Fig. 4 TPA (hardness and cohesiveness) and puncture (firmness) measurement of herring during ice storage. RSD stands for relative standard deviation

The correlation between instrumental texture parameters and storage time (days in ice) was analyzed and shown in

Table I. As noticed from Table I, data from batch 4 was omitted due to very few samples (only 2) of this batch. No

significant correlation between instrumental texture parameters and storage time was found except for the firmness of the data from all three batches 3, 4, and 5. However, it should be noticed that the correlation of firmness and time of batch 3 and 5 were insignificant and controversial, which is negative correlation for batch 3 and positive for batch 5.

TABLE I
CORRELATION BETWEEN INSTRUMENTAL TEXTURE PARAMETERS AND DAYS IN ICE

Texture parameters	Computed values of correlation r		
	Batch 3	Batch 5	Batches 3, 4 and 5
Hardness	0.824	0.696	0.621
Cohesiveness	0.091	0.633	-0.008
Firmness	-0.086	0.905	0.651*

* significant at 5% (two-tailed test)

Correlation between consistency of whole raw fish evaluated by QIM and the instrumental texture parameters was not found (Table II).

TABLE II
CORRELATION (r) BETWEEN SENSORY AND INSTRUMENTAL TEXTURE PARAMETERS OF HERRING STORED IN ICE

Instrumental texture parameters	QIM Consistency
Hardness	-0.081
Cohesiveness	-0.817
Firmness	-0.062

If there was any significant correlation, the r values would be marked with * (significant at 5%), ** (significant at 1%), or *** (significant at 0.1%).

There was difference between batches (Fig. 5) when measured with the e-nose. Batch 3 gave higher responses for all sensors than the other two batches. However, Fig. 5 shows the overall trend that e-nose responses for CO, SO₂, NH₃, and H₂S volatile compounds increased during storage time. There was a drop in responses of day 9 (batch 3) for all sensors, that was caused by some disconnection of the container lid when operating the FreshSense. Therefore, data of day 9 (batch 3) was kept out of the further PCA analysis. The measurements were more precise at high values of responses (results not shown).

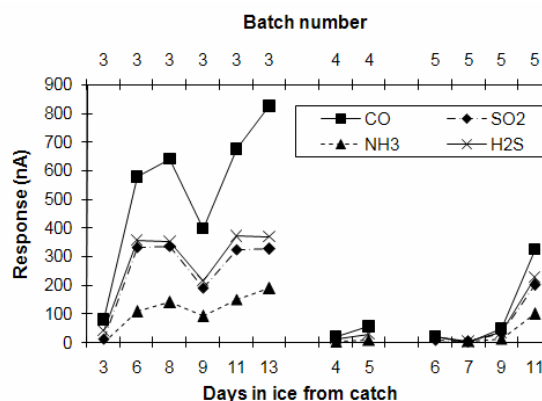


Fig. 5 Electronic nose measurement results of herring stored in ice

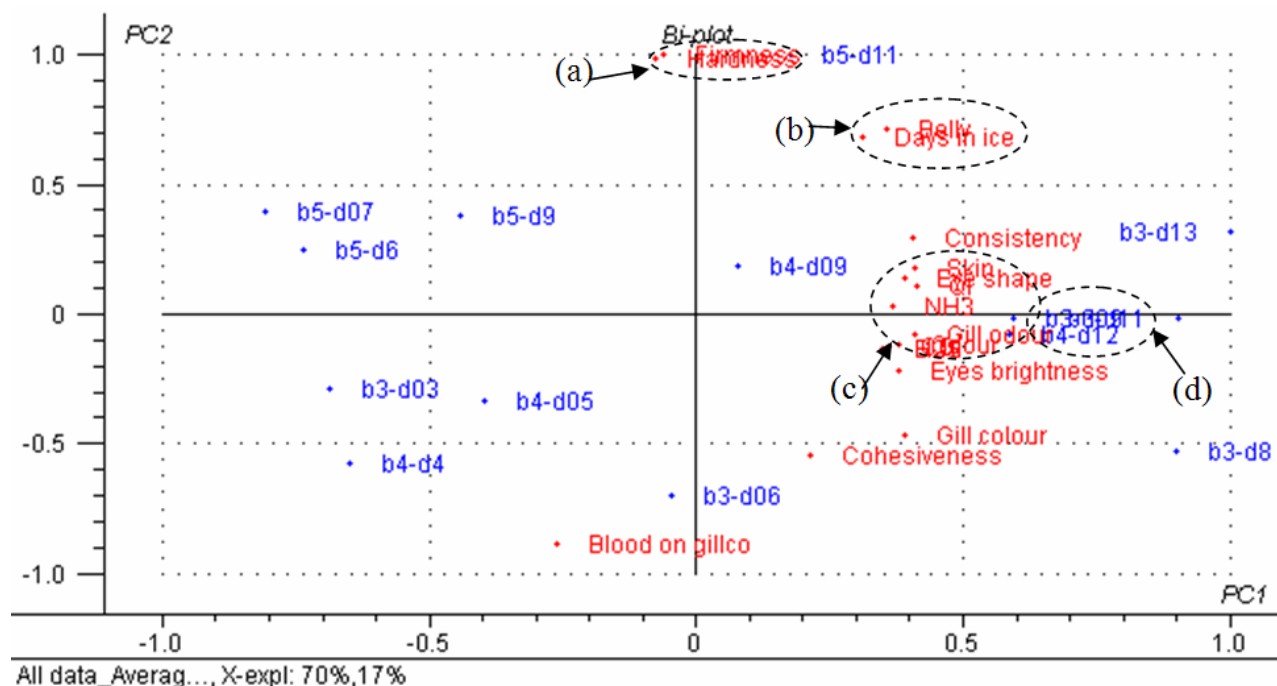


Fig. 6 PCA bi-plot of sensory evaluation, instrumental texture measurements, and electronic nose measurements during storage time, using full cross validation. (a): Hardness and Firmness; (b): Belly and Days in ice; (c): Skin, Eye shape, QI, Gill odour, Odour, NH₃, H₂S, SO₂, and CO; (d): b3-d13 and b4-d12. For the scores: letter "b" follow by a digit is the batch number-letter "d" follow by 2 digit number is days after catch

The PCA bi-plot (Fig. 6) shows that the data of fresh fish was located on the left side of PC1 (explaining 70% of the variance). With storage time, the data moved to the right side of this PC. It is obvious that the same batch gave the same pattern of results even in different methods of freshness assessments. The results show that batch 5 was of better quality than batches 3 and 4, batch 3 was the worst. All the odour attributes of QIM (Odour and Gill odour) and e-nose measurement variables (NH_3 , H_2S , SO_2 , and CO) are located closely to each other on the right side of PC1.

IV. DISCUSSION AND CONCLUSION

The obtained correlation ($R^2 = 0.759$) of the linear relationship between the QI and storage time was higher than the one studied by Martinsdóttir and others [7] ($R^2 = 0.740$). The slope and intersection of this relationship are also different from that study [7]. It might be caused by the difference between the studied materials (catching seasons, catching grounds, fish handling, etc.). Nielsen and Hyldig [21] have indicated that seasons and onboard handling have clear effects on the quality of whole herring stored in ice.

The low values of most QIM attributes at day 7 (Fig. 2) might also be explained by the difference between the studied batches (in catching areas, chilling on board and handling before arrival to the laboratories).

The reason for not observing the increase in scores of descriptor "Blood on gillcover" might be because the QIM scheme just gives the scores based on the area of blood on the gillcover, which does not change during storage. The results could change if the given scores were based on the colour of the blood. Other authors [21] suggested adjusting the range for this attribute.

Descriptor "Belly" could not reach maximum score. It is possible that the belly was not "burst" by the time the whole fish became unfit for human consumption. Therefore it might be better if the maximum score of this attribute is replaced by a higher level of belly softening through storage time. It was found elsewhere that this attribute did not relate to storage time for tank stored herring, but iced fish [21].

Compared to other fish species, the gill colour of herring might change differently by storage time (see also pictures in QIM manual by Martinsdóttir and others [7]). It might cause the difficulty to recognize the difference between days of storage after day 8. There was some suggestion from the judges that it would be better if the scheme had higher maximum score (wider range of scores) for this attribute. Nielsen and Hyldig [21] recommended to use this descriptor for iced herring, but not for tank stored herring.

Those above-mentioned attributes might explain why the QI could not obtain the maximum value at the end of the storage time.

For texture measurements, the variation of the data can be explained by the differences between individual fish. Tryggvadóttir and Olafsdóttir [13] also reported a great individual variation in destructive TPA test measurements of

deskinning haddock fillets.

Higher values of hardness and firmness of batch 5 indicate that this batch had better raw material. It is in a good agreement with the results from the sensory methods of evaluation in this study and in [18], where batch 5 was evaluated or measured of higher freshness quality. It might be caused by the difference in handling of materials before arrival at the laboratories.

As there is some inconsistency in the correlation of firmness and storage time among the batches, the significance of positive correlation between the firmness of all the three batches and time should be rechecked by more measurements.

It should be considered that the texture measurements in the texture analyzer were performed with whole fish with bone and skin on as the same way performed in texture evaluation by QIM. It is not surprising when there is no correlation between instrumental texture and QIM consistency as correlation between instrumental texture parameters and storage time was not found either. The correlation between sensory and instrumental texture parameters might exist but could not be observed in this study. It might be clarified with more measurements. Sveinsdóttir and others [11] also found non-significant negative correlation value between instrumentally measured hardness and QIM for salmon; however the samples for the instrumental test were without bone and skin.

Difference in e-nose responses of batch 3 from batches 4 and 5 can be explained by the fact that herring from batch 3 was caught and delivered from different place than the other two batches, and that there was maybe some abuse in storing and handling of the raw material. In a study on cod fillets by Di Natale and others [22], there was a variation in response of the sensors for different batches due to difference in handling, which caused different spoilage rate.

The higher accuracy of e-nose measurements at high response values indicates that the e-nose is more precise when used to measure/detect above certain level of volatile compounds. That phenomenon is quite understandable because the concentration of volatile compounds in fresh fish was under the detection limit of the instrument used. All these show that the e-nose can be used to detect the onset of spoilage. However, it can not be used to evaluate the freshness at early stages of storage, as it is not sensitive in distinguishing the freshness degree at the first days in ice.

The results from the PCA bi-plot (Fig. 6) indicate the effect of batches' origin, storage and handling conditions on the quality of herring. Close locations of QIM odour descriptors and e-nose measured parameters again shows that the e-nose is sufficiently sensitive to be used to detect the spoilage of fish.

In summary, QIM is a promising method. It would give better results of freshness and shelf life estimation of herring stored in ice if some of the attributes are revised. This method is easy to used, fast and the most practical as it can be performed earlier in the production chain for the whole raw fish. Shelf life of herring in ice could be predicted by QIM

with ± 2 days using 5 herring per lot.

Significant correlation was not found between sensory and instrumental texture parameters. It might be clarified with more measurements. However, it is not clear if instrumental texture measurements are suitable for freshness evaluation of whole herring, as the results depends a lot on individual of fish and other factors (such as biological state of fish before capture, handling condition, the choice of tests, etc. [6]).

Electronic nose shows to be a strong tool in detecting spoilage onset or some abuse in storing or/and handling conditions as it is very sensitive to small changes in volatile compounds above certain concentration.

APPENDIX

QUALITY INDEX METHOD (QIM) SCHEME FOR HERRING [7]				
Quality parameter	Description	Score		
Appearance	Skin	Very shiny	0	
		Shiny	1	
	Mat	Mat	2	
		Blood on	None	0
		gillcover	Very little (10-30%)	1
	Some (30-50%)		2	
	Consistency	Much (50-100%)	3	
		Hard	0	
		Firm	1	
	Belly	Yielding	2	
Soft		3		
Firm		0		
Soft		1		
Odour	Burst	2		
	Fresh sea odour	0		
	Neutral	1		
	Slightly secondary odour	2		
Eyes	Brightness	Strong secondary odour	3	
		Bright	0	
	Somewhat lustreless	1		
Shape	Convex	0		
	Flat	1		
	Sunken	2		
Gills	Colour	Characteristic red	0	
		Somewhat pale, non-glossy, opaque	1	
	Odour	Fresh, seaweedy, metallic	0	
		Neutral	1	
		Some secondary odour	2	
Strong secondary odour	3			
Quality Index		0-20		

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