Electronic Nose Odor Evaluation of Salmon Fillets Stored at Different Temperatures

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ABSTRACT

Current inspection of salmon quality relies on sensory evaluation, which is subjective and difficult to quantify. The purpose of this study was to obtain predictive models of odor changes of salmon fillets stored at different temperatures using an electronic nose (EN) and sensory evaluation data.

Fresh Atlantic salmon fillets were stored at 1.8°, 7° and 11.7°C. Fillets were evaluated for odor attributes by an EN with twelve conducting polymer sensors and a trained sensory panel. Two variable temperature storage studies were done to test the predictive models of odor evaluation.

The response of the sensors to sample headspace volatiles was acquired and analyzed with discriminant function analysis. Results showed good correlations of EN data with both sensory grades and storage time. Variable temperature storage studies demonstrated that the discriminant functions obtained in this study were able to predict sensory grade of salmon fillets from EN data with classification rates higher than 82%.

This study suggested that the EN could correlate the odor of salmon fillets with storage time and with grades from sensory evaluation by using discriminant analysis as the pattern recognition technique.

INTRODUCTION

Fresh salmon of high quality is a valuable commodity worldwide. In 1992 the world commercial catch of salmon was 1,478,000 metric tons, which increased to 2,101,000 metric tons in 1996. In 1996 the United States (US) commercial landings of salmon represented 20% of the world production, with 398,000 metric tons valued at \$369 million. The same year, the US imported \$305 million of salmon, the 4th largest imported fishery product by value. In 1996 salmon was the most important fishery product of export for the US, which generated \$469 million [1].

Current inspection of salmon quality relies on sensory evaluation by inspectors who evaluate the fish for visual, smell and texture attributes. Subjective evaluations make current inspections susceptible to error, difficult to quantify and to compare with

standards worldwide. Moreover, chemical analyses are seldom used by the salmon industry due to the complexity and length of methods. Therefore, there is a need for objective and rapid methods to evaluate the quality of raw salmon that can assist in the development of common standards between the industry, government and international markets.

The odor of seafood products has been widely used as one of the main indicator of quality since ancient times [2]. Fresh seafood has been defined as fish that exhibits a clean, natural odor and physical characteristics representative of the species in good condition [3]. Researchers have tried to find a chemical analysis that can be correlated to that clean, natural odor and that could be used as an index of quality to evaluate seafood products. Some of the methods considered were trimethylamine oxide [4], volatile amines [5], ammonia and total volatile nitrogen [6], hypoxanthine [7], ethanol [8], among others.

Recent developments of sensor technology and electronic noses (EN) have many potential applications in the food industry [9]. Even though EN is a rapid and objective method that could be used to quantify odors, little work has been published which shows correlation of EN sensor outputs and sensory results in seafood products. In the food area, EN has been applied to the evaluation of odor of shrimp [10], monitoring of haddock and cod freshness [11], recognition of fish storage time [12], quality estimation of ground beef [13], monitoring the flavour and aromas of beer and its raw materials [14], [15], classification of grains [16], volatiles of fresh squeezed orange juice [17], among other studies.

The objectives of this study were 1) to measure and obtain predictive models of odor changes of salmon fillets stored at different temperatures with an EN; 2) to correlate these objective measurements with sensory evaluation data; and 3) to test the predictive models with salmon fillets stored in variable temperature environments.

METHODS

SALMON SAMPLES AND STORAGE CONDITIONS

Atlantic salmon (<u>Salmo salar</u>) fillets (1.5-2 kg each) from Chile were obtained fresh, within 48 hrs of harvest. Fillets were cut into three pieces from head to tail. The portion closest to the head was used for this study. The portions were stored in cold rooms set at: 1.8°, 7° and 11.7°C, and kept for 10, 7 and 5 days, respectively. Six fillet portions (replicates) were used for each storage temperature.

Two variable temperature storage studies were also done to test predictive models for odor changes from the discriminant functions. The 1st set of fillets was kept at 1.8°C for the 1st day, then at 11.7°C during the 2nd and 3rd days, and at 1.8°C for the rest of the study until day 7. The 2nd set was kept at 1.8°C for the 1st two days, then at 11.7°C during the 3rd day and at 1.8°C for the rest of the study until day 10.

Moisture content of the fillet portions was measured in triplicate at days 1, 4, 7 and 10 during storage using the oven method. Water activity (a_w) was measured in duplicate using a Rotronic Hygroscop DT (Rotronic, Huntington, NY).

SENSORY EVALUATION

The odor of the fillet portions was analyzed by a 6-member trained sensory panel. Panelists were trained before the study with salmon fillets obtained from the same supplier using a 10-point scale, where 1 = mild, seawater and typical fresh fish odor, and 10 = putrid offensive odor. Values between 2 and 3 were described as mild fishy odors, between 4 and 5 as stronger less pleasant fishy smell, 6 and 7 as souring fishy smell, and above 8 were described as strong sour, rancid and putrid odors. Samples were evaluated for odor every day during the study. All 6 panel members smelled the fillets together and reached a common decision.

The USA Food and Drug Administration (FDA) evaluates the odor of fishery products based on 3 categories: class I, class II and class III [18]. The 10-point sensory scale used in this study was condensed to the 3 FDA classes. Class I odor was samples with sensory grade from 1 to 4 (named grade 'A' in this study); Class II odor ranged from 5 to 7 (grade 'B'); and Class III odor ranged from 8 to 10 (grade 'C').

ELECTRONIC NOSE MEASUREMENTS

An e-NOSE model D (EEV Inc, UK) equipped with 12 conducting polymer sensors was used to quantify the sensor responses to odor changes in salmon fillets during storage. A 60-g piece of salmon fillet was taken out of the cooler one hour prior to analysis to let the sample equilibrate to room temperature (21.6 to 22.6°C). Six replicates were analyzed on each day for each temperature storage, and 3 replicates were done for both of the variable temperature studies. The piece of salmon was placed in a 140-ml beaker and placed in the sampling vessel of the EN. Every day prior to the experiments the EN was turned on and compressed air was passed through the sensors for 20 minutes. For each replicate, the vessel and head were purged with compressed air for 2 and 4 minutes respectively. During head purging, the sample volatiles were equilibrating in the headspace of the vessel. Then, sensor response data was acquired for 3 minutes. Total analysis time for each sample took 9 minutes. Readings at 3 minute exposure of the sensors to the samples were used for data analysis.

DATA ANALYSIS

Analysis of variance (ANOVA) was used to test differences in moisture content and a_w during storage. Sensor readings and sensory data were analyzed in Statistica for Windows (Ver. 4.5, StatSoft Inc., Tulsa, OK) using discriminant function analysis (DFA) to develop predictive models for classification of samples based on the three odor groups (grade A, B, or C), and storage time. The 12 sensor outputs were reduced to 2 discriminant functions. Correct classification rates and the coefficients for each function were obtained. The sensor data from the two variable temperature studies were not included in the data set to obtain the discriminant functions for the model. Instead, these were used for validation, i.e. to determine whether the discriminant

functions provided reliable means of classifying these salmon fillets into one of the sensory grades (grade A, B, or C).

RESULTS AND DISCUSSION

Conducting polymer sensors can respond to changes in humidity of the headspace of the sample being analyzed [19], [20]. This study monitored the humidity of the samples analyzed. Moisture content and water activity of the salmon fillets did not change with storage time for any of the three temperature storage conditions, and for the two variable temperature studies (Table I). ANOVA could not detect differences (p=0.05). The average moisture content of the salmon fillets was 72% (wet basis). The average water activity was 97.4%.

Table I. Moisture content (% wet basis) and relative humidity (%) of salmon fillets during storage at

different temperatures. ($\pm = \text{std. deviation. } n = 3$).

Storage time		Storage Temperature						
(days)		1. 8°C	7°C	11. 7°C	Var. temp. 1	Var. temp. 2		
1	% H₂O	72.5 ± 1.85	68.9 ± 1.08	71.6 ± 1.94	73.7 ± 0.30	72.3 ± 2.38		
•	% RH	97.4 ± 0.14	97.1 ± 0.00	97.3 ± 0.21	97.2 ± 0.07	97.2 ± 0.07		
4	% H₂O	72.7 ± 1.50	70.8 ± 1.25	72.4 ± 1.07	73.8 ± 0.54	72.8 ± 0.14		
7	% RH	97.4 ± 1.21	97.3 ± 0.21	97.2 ± 0.07	97.4 ± 0.14	97.5 ± 0.07		
7	$^{\text{M}}$ H ₂ O	72.1 ± 0.53	70.9 ± 0.89	-	70.7 ± 1.36	69.4 ± 0.72		
,	% RH	97.4 ± 0.14	97.3 ± 0.07	•	97.4 ± 0.21	97.3 ± 0.07		
10	% H₂O	73.6 ± 0.26	-	-	_	73.1 ± 1.38		
10	% RH	97.4 ± 0.14	-	-	-	97.4 ± 0.07		

(%RH measured at $24^{\circ} \pm 0.5^{\circ}$ C)

Figure 1 shows the DFA results correlating EN readings to sensory data at each storage temperature. The twelve sensor outputs were reduced to two discriminant functions to produce points which were mapped on the two-dimensional plots. For the three storage temperatures 1.8°, 7° and 11.7°C, DFA clearly separated the data into the three grades A, B, or C. The correct classification rates for the discriminant functions were 93.3%, 92.9% and 96.7% for the 1.8°, 7° and 11.7°C storage temperatures, respectively (Table II). Results from the DFA of the lowest storage temperature data (1.7°C) show some overlap of sensory grades. Data classified as grade A were uniformly distributed, forming a circular cluster of data. However, samples classified as grade B and C are spread out in long elliptical clusters, overlapping with each other and with the grade A cluster. This overlap could be due to the fact that sensory analysis was carried out by panelists that may have misclassified some samples, since change in smell is not as drastic at low temperatures. For the 7° and 11.7°C storage temperatures, separation into the three sensory grades was very clear. As expected, the distance between the cluster from grade A and grade C was greater when compared with grade B.

Table II. Correctly classified cases obtained from the classification matrix for the DFA of EN readings

compared with sensory grades. (Values are % of correctly classified samples)

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Class (sensory score)	1.8°C (n=60)	7°C (n=42)	11.7°C (n=30)	All temperatures ¹ (n=132)	Variable temperatures ² (n=51)
A (1-4)	95.2	88.9	100.0	79.2	86.7
B (5-7)	91.7	100.0	91.7	90.0	83.3
C (8-10)	83.3	94.4	100.0	90.0	79.2
Overail	93.3	92.9	96.7	84.1	82.4

n = number of EN readings used to obtain the discriminant functions

Data from the three storage temperatures were pooled together and analyzed with DFA. The correct classification rate in this case was 84.1%. As expected, the correct classification rate is lower since there is increased variability due to the combination of all the odors from each temperature. During sensory evaluation of the salmon fillets, panelists detected differences in odors between temperatures. The putrid odor at 1.7°C which was given a score of 8 or 9 was different from the putrid odor at 11.8°C with the same sensory score. At different storage temperatures there will be selective growth of different types of microflora (psychrophilic and mesophilic microorganisms), and the metabolites from them will be different. In addition, reaction rates at the three temperature storage conditions are different. At the highest temperature condition (11.7°C), panelists detected a stronger rancid odor compared to those at lower temperatures.

Variable temperature storage studies demonstrated that the discriminant functions obtained in this study were able to predict the sensory grade of salmon fillets from EN data with an accuracy of 82.4%. The functions used to perform the validation of the data were those obtained by pooling the three storage temperatures data together. From the 51 EN readings from the two variable temperature storage studies, 42 readings were correctly classified based on sensory grades given by panelists. This value is close to the 84.1% correct classification rate obtained in the model. Therefore, 17 from every 20 fillets evaluated using the predictive model developed will be correctly classified according to sensory grade.

Salmon odor was also changing with storage time. At the lowest temperature (1.7°C), some panelists could not detect differences in odor between consecutive days. However, the EN was able to detect differences between the odor of salmon at the different days of storage. DFA was used to calculate two discriminant functions that described the correlation between EN readings and storage time for each storage temperature data. The correct classification rates for the discriminant functions were 93.3%, 97.6% and 100% for the 1.8°, 7° and 11.7°C storage temperatures, respectively (Table III). Figure 2 shows a clear discrimination between days in storage. In all three temperatures the cluster for day one is further apart than the other days. All other days formed individual clusters with little or no overlap, meaning that there were distinct differences in the sensor readings for each day of storage.

¹ data for 1.8°, 7° and 11.7°C pooled together

²data from both variable temperature studies pooled together

Table III. Correctly classified cases obtained from the classification matrix for the DFA of EN readings

compared with storage time. (Values are % of correctly classified samples).

Groups (storage time in days)	1.8°C (n=60)	7°C (n=42)	11.7°C (n=30)
1	100.0	100.0	100.0
2	100.0	100.0	100.0
3	100.0	100.0	100.0
4	100.0	100.0	100.0
5	83.3	83.3	100.0
6	83.3	100.0	-
7	100.0	100.0	-
8	83.3	-	-
9	100.0	-	-
10	83.3	-	-
Overall	93.3	97.6	100.0

n = number of EN readings used to obtain the DFA functions

This study showed that the EN was able to correlate the odor of salmon fillets with storage time and with grades from sensory evaluation by using DFA as the pattern recognition technique. These results could be used to develop methodologies to assist in the objective and repeatable quality evaluation of salmon. This method has potential in industrial and regulatory application where rapid response, no sample preparation, no requirements for chemicals, and no technical expertise to run the system are required.

This study showed the feasibility of using EN technology to evaluate odors of salmon fillets. However, further work is needed to accumulate extensive data sets that could be used to predict the sensory grade of salmon taking into account different species, origins, season of harvest, age of fish, growing environment (aquaculture or wild), etc. It is expected that including all these variables will affect the correct classification rate. It is also crucial to test the transportability of the model from one EN system to another. This is critical in demonstrating the feasibility of using EN based inspections and evaluations in commercial settings.

REFERENCES

- 1. USDC. 1997. Fisheries of the United States, 1996. "Current Fishery Statistics No. 9600." Washington, DC: U.S.D.C. U.S. Government Printing Office.
- 2. Botta, J.R. 1995. Evaluation of Seafood Freshness Quality. New York, NY: VCH Publishers Inc.
- 3. Perkins, C. 1992. The Advanced Seafood Handbook. Rockland, ME: Seafood Business Magazine.
- 4. Hebard, C.E., Flick, G.J., and Martin, R.E. 1982. "Occurrence and significance of trimethylamine oxide and its derivatives in fish and shellfish," in *Chemistry*

- and Biochemistry of Marine Food Products, R.E. Martin, F.G. Flick and D.R. Ward, eds. Westport, CT: AVI Publishing Co., pp 149-304.
- 5. Storey, R.M., Davis, H.K., Owen, D., and Moore, L. 1984. "Rapid approximate estimation of volatile amines in fish." J. Food Technol. 19, 1-10.
- 6. Halland, H. and Njaa, L.R. 1988. "Ammonia (NH₃) and total volatile nitrogen in preserved and unpreserved stored whole fish." J. Sci. Food Agric. 44, 335-342.
- 7. Mulchandani, A., Luong, J.H.T., and Male, K.B. 1989. "Development and application of a biosensor for hypoxanthine in fish extracts." Anal. Chim. Acta 221, 215-222.
- 8. Kelleher, S.D. and Zall, R.R. 1983. "Ethanol accumulation in muscle tissue as a chemical indicator of fish spoilage." J. Food Biochem. 7, 87-92.
- 9. Corcoran, P. 1993. "Electronic odour sensing systems." Electronics and Communication Engineering J. 5(5), 303-308.
- 10. Balaban, M.O. and Luzuriaga, D.A. 1996. "Automated quality evaluation of shrimp." Food Quality 5, 56-66.
- 11. Olafsson, R., Martinsdottir, E., Olafsdottir, G., Sigfusson, S.I., and Gardner, J.W. 1992. "Monitoring of fish using tin oxide sensors." in *Sensors and Sensory Systems for an Electronic Nose*, J.W. Gardner and P.N. Bartlett, eds. Kluwer Academic Publishers, NATO ASI Series. Volume E212, pp. 257-272.
- di Natale, C., Brunink, J., Bungaro, F., Davide, F., d'Amico, A., Paolesse, R., Boschi, T., Faccio, M., and Ferri, G. 1996. "Recognition of fish storage time by metalloporphyrins-coated QMB sensor array." Meas. Sci. Technol. 7, 1103-1114.
- 13. Winquist, F., Hörnsten, E.G., Sundgren, H., and Lundström, I. 1993. "Performance of an electronic nose for quality estimation of ground meat." Meas. Sci. Technol. 4, 1493-1500.
- 14. Pearce, T.C., Gardner, J.W., Friel, S., Bartlett, P.N., and Blair, N. 1993. "Electronic nose for monitoring the flavour of beers." Analyst 118, 371-377.
- 15. Tomlinson, J.B., Ormond, H.L., and Sharpe, F.R. 1995. "Electronic aroma detection in the brewery." J. of the Amer. Soc. of Brewing Chem. 53(4), 167-173.
- 16. Börjesson, T., Eklöv, T., Jonsson, A., Sundgren, H., and Schnürer, J. 1993. "Electronic nose for odor classification of grains." Cereal Chem. 73(4), 457-461.
- 17. Bazemore, R., Rouseff, R., and Sims, C. 1996. "Comparison of fresh squeezed orange juice analysis by electronic nose, sensory panel and GC FID." The 3rd International Symposium on Olfaction and Electronic Nose. Nov. 3-6, Miami, FL.
- CFR. 1997. "Code of Federal Regulations. Title 50, Wildlife and Fisheries" Part 265. Washington, DC: The Office of the Federal Register, National Archives and Records Administration, U.S. Government Printing Office.
- 19. Bartlett, P.N., Elliot, J.M., and Gardner, J.W. 1997. "Electronic noses and their application in the food industry." Food Technol. 51(12), 44-48.
- Shurmer, H.V. 1990. "An electronic nose: a sensitive and discriminating substitute for an mammalian olfactory system." IEEE Proceedings 137-G(3), 197-204.

Figure 1. DFA of salmon odor based on sensory grades and EN readings

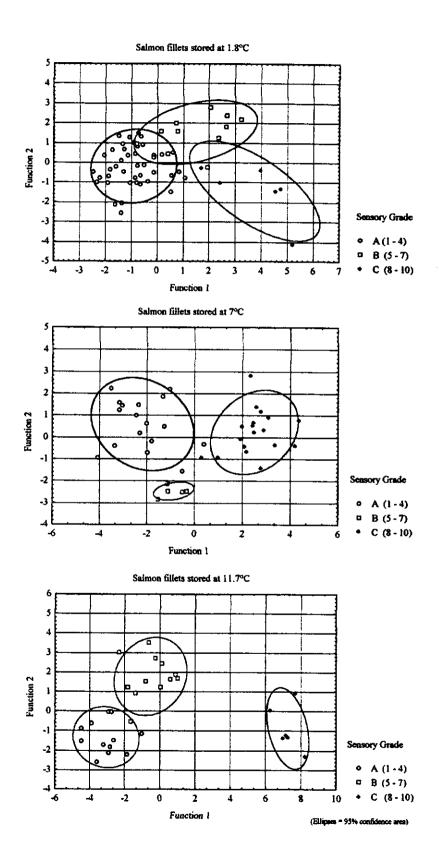


Figure 2. DFA of salmon odor based on storage time and EN readings

